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ONTARIO HIGH SCHOOL CHEMISTRY



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ONTARIO HIGH SCHOOL CHEMISTRY

PUPILS' TEXT-BOOK

Authorized by
The Minister of Education for Ontario

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PREFACE

This book is published in two parts, in accordance with what is believed to be good pedagogical practice, viz.: To enable pupils to gain a knowledge of chemistry by *doing chemistry*, not simply by "getting it up." For this purpose it is intended that both parts of the book shall be in the hands of the scholars; and that when a topic is taken up the practical exercises relating to it shall be worked, as directed in the Manual, and the observations *necessary for the lesson* shall be recorded for reference. After the notes relating to the subject have been satisfactorily completed, it is expected that the teacher shall discuss the results with the class in a systematic way, and shall guide the pupils to proper conclusions in accordance with chemical laws and principles. In this connection the descriptive part of the Text-book will come into service.

Manifestly the pupils' note-book will be an important part of his material outfit, for it will form the connecting link between the exercises of the Manual and the description of the Text.

The Chemistry of the Middle School should serve a double purpose for the pupil who properly studies it. One of these aims at the development of that mental attitude called the scientific mind which investigates, weighs evidence, and forms judgments based on reason. The other consists in imparting to the student such a knowledge of the facts, the principles and the methods of the science that he will be able either to acquire further information of the same kind by independent reading, or to take up a more advanced course of chemical study.

Without doubt, the educational function is the more important one; and, while the two objects have some elements in common, there is yet divergence enough between them to cause hesitancy, at times, as to which of two courses is the preferable one to follow. Under such circumstances there must be some compromise between what is best and what is possible, especially when the work has to be curtailed to meet the requirements of a time limit.

It has been thought best to treat the subject in accordance with modern theory, and to introduce from the first the ideas and the terminology needed for that purpose, in order that the student may not have to discard, at a latter period, what he learns regarding chemistry in the High School. For these reasons the method of treatment and the choice of material will vary somewhat from those hitherto adopted. The present equipment of the schools, the relations of science to daily life, and the character and aims of secondary education in the province have all been considered in determining what shall be taken up in the course, and how it shall be dealt with.

Chemistry, though more particularly concerned with concrete materials, has almost the logical definiteness of mathematics, so that educationally it is an excellent subject for securing closeness of observation, accuracy of reasoning, clearness of judgment and exactness of expression. The attraction that the study has for most pupils of secondary school age is easily accounted for by the opportunity it affords to solve problems by experiment, and by the easily observed phenomena that accompany chemical activity. The quantitative character of the reactions, and the fixed laws that govern chemical change, enable the teacher to take advantage of this partiality for the subject to secure valuable educational results, especially when pupils are at the age at which they are just passing beyond the stage of thinking in terms of the concrete.

It is assumed in this book that pupils have taken the Lower School Physics; and work that would be a repetition of that formerly done has been omitted. It is also taken for granted that there will be an instructor competent to direct the study, to drill on important points, to put stress where it is required, and to fill in details which he may think necessary. A text-book is of value as a guide to the work, as economising time for both master and students by system and condensation; but it is not a treatise embodying all that is known of the subject. It can not, in any sense, replace the teacher, because it is without personality, it can inspire no enthusiasm, and it lacks all emphasis. The experiments in the Manual are generally suitable for students' practice; but the varying facilities for this work in different schools will doubtless lead to some of the experiments being done by the teacher or by pupils under his direction. For this purpose the selections will not be the same in all cases, so the choice has been left with the teachers concerned. The text-book assumes these experiments to have been completed, and the observations recorded. The results are briefly discussed, their relationships pointed out, and necessary information supplied. The practical work done by the student must be constantly supervised by the teacher, because the value of an experiment does not lie in the noise and flare that it produces, but in what the student gets out of it that he can apply to the problem he is solving or to the investigation he is making.

The following principles should be observed regarding experimental work in class:

1. There should be no random work; every experiment should be undertaken for one definite purpose, *and only one*, and the student should know what problem he is seeking to solve, and what he is to note among the results observed. For this purpose, he should receive directions in the form of questions or hints. Further, it is all important that the experimenter should rely entirely on his observations, and that he should not discount his own work by having his mind made up regarding what should occur.

2. The accurate use of language should be rigidly insisted on to express exactly what is intended, neither more, nor less, nor any-

thing else. Slovenly expression is no more to be tolerated than slovenly work.

3. Whatever tends to divert attention from the one thing sought should be avoided. All diffusion of either thought or effort is wasteful and injurious. If a second result of an experiment is wanted for some other purpose, reference should be made to the notes, or the whole repeated, but with the new requirement as the object.

4. The notes that record the conditions of the experiment and the phenomena observed should be written by the pupils themselves, at the time of making the experiment, and without dictation or suggestion from the teacher. The note-book should be a register of the student's experiences, and entries should be made in it while the matters being described are still fresh in mind.

The value of an experiment is only slightly in the doing of it, mainly its worth lies in the discussion of the observations. The questions that accompany the directions for the experiments in the book are intended to be only suggestive, for such questions must of necessity be general in their character. The teacher should, therefore, take up the consideration of the problem from the point of view of the pupils' requirements and experiences as shown in what they have derived from the work done.

It is believed that most pupils taking this **Middle School Course** will get no further instruction in Chemistry; hence an effort has been made to connect this particular school work with the activities of life. This should be one of the main vitalising elements of the subject, and no opportunity should be missed of emphasising such relationships and applications, especially in connection with local conditions and industries. While these are important in their way, neither the commercial aspect of the study, nor mere knowledge of the details of the science, should be permitted to displace the effort to develop that attitude of mind which causes the pupil to observe accurately, to take account of essential conditions, and to draw proper inferences from them.

The sign of equality used to express chemical action has been, at times, replaced by an arrowhead. The latter is now a recognised symbol of chemical notation; students, therefore, should be familiar with its use. In this book it is employed in cases in which emphasis is directed to changes in substances rather than to equality of masses. If any excuse were required for its introduction, a sufficient one would be formed in its common use to express reversible reactions.

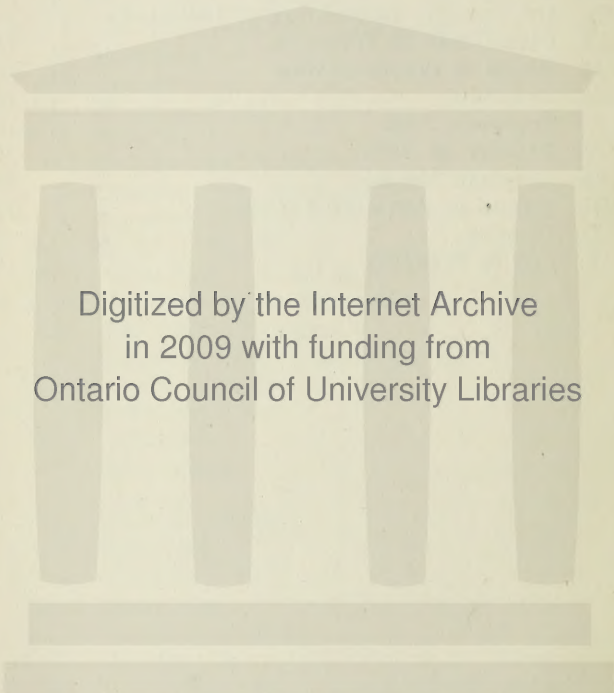
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CHEMISTRY

CHAPTER I

MATTER AND ENERGY

In the physical world man has to do with two things: **Matter and Energy**. **Chemistry** has for its province the investigation of the composition, properties and relations of the various kinds of matter, while **Physics** is concerned mainly with energy. The two domains, however, overlap, because changes in matter are generally accompanied by changes of energy and the chemist must take cognisance of both, or else he will not be dealing with all the elements of the problem.

Matter occupies space, or has extension; it is affected by gravitation, and, as a consequence, has weight; and it lacks the capacity to originate or alter motion, except under the influence of external force.

The term **Substance** is applied to matter that is all of the same kind, or that is of the same composition; for example, water, iron, lime and marble. A **Body** is a portion of matter separate from other portions of the same substance, as a lump of iron, a pailful of water, a litre of air or a fragment of glass. **Mass** means the quantity of matter in a body.

Energy is the capacity to produce motion. This means the ability to change the position of a body, to alter its motion either in direction or rate, or to set its minute parts (called molecules) in vibration.

The forms of energy met with in elementary chemistry are chiefly: (1) Energy of position. Coal in presence of oxygen, one of the gases of the atmosphere, is capable of yielding heat and light by the chemical action that may occur between the two; but coal in presence of nitrogen, the other gas of the atmosphere, has no such capacity of giving off heat. Some other examples of energy of position are afforded by the mixture called gunpowder, sulphuric acid in presence of zinc or magnesium, coal gas mixed with oxygen, and the gases that form water (oxygen and hydrogen) when in contact. (2) Energy of vibratory motion of particles, known as **Heat**. There is perhaps no commoner manifestation of change of energy in connection with chemical action than the emission or absorption of heat. (3) Energy of the electric current. The decomposition of water by the method of electrolysis, and the action in a common battery cell, are illustrations of the relation that some chemical changes bear to this form of energy. (4) Emission or absorption of light waves. Artificial lighting of houses by lamps, candles or gas, and the changes produced in photographic plates and many dyes, when exposed to sunlight, are examples of the connection between light and some of the common chemical actions.

The changes then which matter undergoes in state, or in composition, or in both, are produced in some cases by the application of external energy, as in the boiling of water, the melting of iron, or the "burning" of lime. On the other hand, energy is frequently set free during changes in the condition or the composition of matter; and men take advantage of this property to obtain power for their industrial needs. Thus the engineer, through the agency of water, uses the energy of fuel and air to secure the requisite motion of his machinery.

When coal has become burned, or steam condensed to water through loss of heat, or a zinc plate eaten away in a battery jar, the energy of the substance is said to have run down. Many kinds of matter are in this run-down state, for while energy cannot be destroyed, it may be transferred to other substances, or transformed into some less available state. Thus the coal and air, the steam, and the zinc and acid, may be compared to water stored at a height above sea level; as the coal burns, or the steam condenses, or the zinc changes from the metallic state, or the water flows down toward the ocean, the stored energy is being dissipated.

CHAPTER II

PHYSICAL AND CHEMICAL CHANGE

From the Experiments 1 to 8 in the Manual, we learn that platinum wire, when heated, changed some of its properties temporarily, but that it was not altered to any other substance than platinum. Magnesium, though, underwent a permanent change, for a silvery white, tough, elastic metal was altered to a white powder *that weighed more* than the original metal. Copper, too, when heated with a colourless gas changed from a bright red metal to a black mass that was easily ground to powder; and the black substance was *heavier* than the metal. Nitrate of lead, a white powder, when heated gave off a brown gas and changed to a buff-coloured substance, and this *weighed less* than the nitrate did. Indeed, this separation may be carried farther, for if the substance left in the tube were heated in coal gas, as the black substance derived from the copper was, metallic lead would be left, which would weigh less still than the residue from the first heating. Sugar, when heated, was altered to a black, tasteless, insoluble mass that weighed only about two-fifths as much as the sugar itself did. Oxide of mercury, a brick-red powder, changed to a fluid metal, and something which escaped out of the tube and affected the glowing of the splinter. Water, when made part of an electric circuit, was separated into two colourless gases that differed from each other and from the original substance.

These are examples of **Chemical Changes**. Such

changes are characterised by (1) An alteration in the essential properties of the substance or substances affected. (2) Change of the quantity of matter in the individual substances as indicated by alteration of their weights. (3) Absorption or setting free of energy.

The *essential properties* of a substance are those which distinguish it from all other kinds of matter; in short, any substance is what it is, and not something else, because of its essential properties.

The quantity of matter in the new substance is different from that in any one of those from which it was produced. The black powder formed from oxygen and copper consists of more matter than either the copper or oxygen alone; on the other hand, the solid remaining after the lead nitrate was heated does not consist of as much matter as the nitrate did, because a red gas could be seen passing off from it, and there was loss of weight.

In these cases, and such as these, the copper and magnesium are said to **combine**, or enter into *chemical union*, with the oxygen to form substances whose essential properties differ from those of copper and oxygen, or of magnesium and oxygen as the case may be. The lead nitrate changes in the reverse way, for it is *separated* or decomposed into a coloured gas and a yellowish solid, each of which has properties different from those of the original nitrate and of each other. The copper and oxygen which combined to form the black powder are said to be the *constituents* of that powder. Also the constituents of water are two colourless gases; of nitrate of lead, a coloured gas and a yellowish solid; of oxide of mercury, metallic mercury and a colourless gas.

Substances which we find to be made up of the same constituents, in the same proportions, we find also to have the same essential properties, hence they are the

same kind of matter, though they may exist in different states, and, on that account, may show some different properties. Ice, water, and steam are familiar illustrations of various states of the same kind of matter, because the change from one to the other is dependent on heat, which is not matter; and there is no change of weight when one passes into the other, hence there is no alteration in composition.

Chemical change may be the combining of two or more kinds of matter, as in the case of the burning of magnesium; or the separation of a substance into two or more different ones, as in the decomposition of the oxide of mercury and of water; or in the rearrangement of the components of two or more substances to form new kinds of matter, as when zinc and sulphuric acid act together to produce hydrogen, and marble and hydrochloric acid to form the gas, carbon dioxide.

There are changes of matter and energy which cannot be classed as chemical, yet have to be taken into account in almost every chemical operation. These affect some of the properties of matter, and are related to changes in energy, but they are not marked by alteration of composition. Thus a platinum wire may be heated until it gives out light, yet when it cools it is the same, both in kind and quantity, that it was before the change. It absorbed energy when being heated, and gave it out again to the same extent when cooling. When water is transformed into steam, energy is supplied to it from the source of heat, but that energy is set free when the steam changes back to water, and at no period of the operation does the quantity of matter change. A spoonful of sugar put into a glass of water disappears to the sight, but not to the taste, and the sugar absorbs energy when changing its condition, but there is no change of composition,

for when the water evaporates, the sugar remains in the same quantity and same condition as at first. A glass plate may be ground to powder, but the powder weighs just what the plate did, and it is composed of the same materials in the same proportions as the plate was; it is, therefore, still glass, but in a different state from the plate, and that difference was produced by the application of energy which disappeared as work.

These are some illustrations of **Physical Change**. Such changes require a transfer of energy, but do not produce any alteration of composition. There may be change of state with its accompanying altered properties; but no new matter, in the sense of having different constituents, is formed.

In a general way physical changes are mainly those which are connected with the alteration of position, or of condition of aggregation, or of shape, or of state. A brick may be ground into a thousand little masses, and the change is brought about at the expense of mechanical energy expended as work. A dissolved solid may be formed into crystals, but it gives out heat in the change. A piece of silver may be stamped into a coin, or a drop of molten glass drawn out to a thread, but energy disappears as work in the process. A lump of sulphur exists as a solid, but the absorption of enough of heat energy will cause it to become liquid and more heat will change it into a gas, yet it is sulphur and nothing but sulphur all the while, with all the properties unchanged that mark the distinction between it and any other kind of matter.

While this distinction of chemical and physical change is clear enough in such type cases as those mentioned, it should be pointed out that there is a borderland where physics and chemistry meet and seem to overlap, so that

it is by no means clear to which domain some changes should be assigned. Solution is generally classed as a physical change, but it is very doubtful if such a classification is scientifically correct, especially in the case of substances which can be decomposed by the electric current when they are in solution. An elementary textbook, however, is not a suitable place for the discussion of these problems.

A few common cases of chemical change are those occurring when fuel burns, when wood rots, when milk sours, when metals rust, when foods are changed into animal and vegetable tissues, when air is breathed, when a photograph is made, when soda is mixed with vinegar, and when bread rises.

Some examples of physical change are the following: dissolving of solids, evaporating of liquids, melting of ice or of metals, heating of iron, grinding of solids to powder, magnetising of iron, and bending of wire.

CHAPTER III

ELEMENTS AND COMPOUNDS

It has been found by experiment that copper may be made to combine with oxygen to form a black powder, oxide of copper; and that, by proper treatment, the oxygen may be taken away from that oxide, leaving the original copper unchanged in either properties or quantity. For a hundred years men have been experimenting with oxygen and copper, but no one has found a way by which either may be separated into substances different from itself. Stated in another way, this means that oxygen and copper have never been decomposed as the oxide of copper has been. Similarly oxide of mercury has been decomposed into oxygen and mercury, but it is not possible to separate mercury into other kinds of matter that have properties different from those of mercury. Zinc can be made to act with sulphuric acid, and a new substance is formed from which the zinc can be again recovered, but all efforts to decompose zinc have failed. All kinds of matter may thus be divided into two classes; the members of one class can be separated into other kinds of matter, the members of the other class cannot be so separated. The latter are called *elements*, the former *compounds*.

An *element* is that kind of substance from which a different kind cannot be obtained except by *combining* some other substance with it.

A *compound* is that kind of substance which can be *separated* into different kinds of matter.

A new kind of matter can be derived from an element only by combination.

New kinds of matter can be derived from a compound either by combination or decomposition.

There are about eighty elements known, but only a few are of common occurrence. About twenty-five of them, in their various combinations, make up most of the substances with which we come in contact in daily life.

Elements are divided, for convenience, into two classes, metals and non-metals, the distinction between them depending on certain properties possessed by the former, but not by the latter.

They may also be grouped according to their physical condition at ordinary temperatures; thus, all metals with one exception, and a few non-metallic elements like phosphorus, carbon, and sulphur, are solids; two elements, mercury and bromine, are liquids; and about ten are gases.

Several new elements have been discovered within recent years owing to more accurate means of investigation, and it is almost certain that others will be found in the future. Perhaps, too, some substances now called elements may turn out to be compounds or modified forms of other elements.

CHAPTER IV

MIXTURES, SOLUTIONS AND COMPOUNDS

Mixtures.—If some iron filings be shaken with sugar the result is a mixture from which iron may be drawn with a magnet, or sugar dissolved out with water, but each is unchanged either in quantity or properties. There may, too, be little iron or much in comparison with the sugar, and there may be a great deal of iron in one part of the mixture and a very little in another, the quantity is unimportant so long as both are present and the parts intermingled. Water with a layer of oil floating on it is not a mixture, because there is a sharp boundary with one kind of matter on each side of it, but let them be shaken together so that the globules of oil become distributed through the water, and, for a time, there is a mixture of the liquids.

The characteristics of a mixture are that it shall consist of at least two substances whose parts are intermingled, that it need not be homogeneous, that the components may be present in varying proportions, and that each of the components shall retain its own properties and identity.

Solutions.—If a little sugar be put in a glass of water, it will presently disappear to the sight, but the water will acquire a sweet taste, and if it be evaporated the sugar will remain. A definite quantity of water will dissolve sugar up to a certain amount, that varies with the temperature of the water, but not beyond that limit. A *saturated solution* is one in which the liquid, when stirred,

will, at that temperature, take up no more of the substance being dissolved. Heating a liquid usually increases its solvent power for solids, so that if the temperature of a saturated solution be lowered some of the dissolved substance will separate out in the solid form. Such precipitation may be shown by making, in boiling water, saturated solutions of alum, potassium chlorate, or potassium bichromate, and allowing them to cool. Solutions tend to become homogeneous because liquids of the same kind, but of different densities, diffuse through one another when in contact.

Some liquids are soluble in others, as sulphuric acid, glycerine or alcohol in water; while substances like oils, that are not soluble in water, will frequently dissolve in other liquids such as chloroform, ether or carbon bisulphide.

Many gases are easily dissolved, as ammonia, and hydrogen chloride. A rise in temperature decreases the solvent power of a liquid for gases, while lowering the temperature increases it. With solids the reverse is usually the case and the difference is due to the natures of the substances. Heat increases the already high volatility of a dissolved gas and drives it out of solution, but the solubility of a solid is increased when the cohesion of its particles is made less by heat. The solubility of a gas in presence of its solvent varies directly with the pressure upon it. A solution of a solid in water boils at a temperature above 100° C. and the boiling point of a saturated solution is higher than that of a dilute one; this is equally true of liquids less volatile than water, when dissolved in the latter. When a substance like alcohol, however, that itself boils at a low temperature, is dissolved in water, the boiling point of the solution is lower than that of water alone.

Water solutions of solids generally freeze at temperatures lower than $0^{\circ}\text{C}.$; and since freezing is a process of crystallisation, it causes a separation of the solvent from the dissolved substance. When sea water is frozen and the ice taken off and melted, fresh water is obtained, except for a little salt mechanically entangled in the crystals. The natives of Northern Siberia obtain their supply of salt by concentrating the solution of it in sea water by repeatedly freezing the latter and removing the ice.

The characteristics of a solution are: That the substance dissolved shall be rendered liquid through the agency of the solvent, itself a liquid; that the dissolved substance may be present in any proportion from a mere trace to a maximum limit; that by diffusion the solution becomes homogeneous; that the solution may differ from the solvent in some particulars, as density, boiling point, freezing point and viscosity. While the general facts are as stated here, there are some cases in which the substances are mutually soluble in all proportions, as alcohol and water and glycerine and water.

Ordinarily the term solution is applied only to those substances that either exist as liquids or were formed in the liquid state. This applies to some solids, as colouring matter in glass, and the amalgams. The uniform distribution of one substance through the other could occur only in the liquid condition.

Compounds.—Iron shaken with sulphur forms a mixture in which both ingredients can be detected and from which both can be separated by simple methods; but if iron and sulphur be heated out of contact with air, a compound is formed in which neither iron nor sulphur, as such, is present; yet both enter into the compound, and either may be recovered from it, but only after decom-

posing it by chemical means. It is no longer possible to wash out the sulphur, nor to dissolve it with carbon bisulphide, nor can the iron be separated by a magnet. In the case of sulphuric acid and zinc, Experiment 9, a crystalline solid is formed by the union of a grey white metal and a clear oily-looking liquid, and if they are not present in the right proportions, an excess of one remains. For every 65 parts by weight of zinc there must be 98 of the acid, otherwise part of one of the substances will be left over, so that combination occurs only between certain fixed quantities of the substances. This may be shown by taking about two grams of zinc and placing it in 2 c.c. of hydrochloric acid, diluted one-half. After all action has ceased, drop in some more acid, repeat until the zinc all disappears, then add a few drops of acid and put in another piece of zinc. The new kind of matter that is formed in combination is uniform in its composition. Chemical combination may be described as the union of two or more substances to form a new kind of matter differing in properties from any of its constituents. This difference is due to a rearrangement of the constituents, which takes place only between definite portions by weight of the substances entering into the union, and the compound thus formed is entirely homogeneous.

In mixtures each of the substances retains its identity. In solutions the properties of each substance may be affected by the presence of the other. In compounds the substances that combine lose their identities and cease to have a separate existence. Solutions thus stand between the extremes of mixture and combination; and in the case of *saturation* they show the first quantitative limits which form the most pronounced characteristic of compounds. It is probably not right to say that what takes place when sugar is put

into water differs only in degree from that which occurs when it is put into sulphuric acid; the actions differ in kind, but they have some things common that are entirely lacking in the case of sugar in coal oil.

If a mixture of iron filings and sulphur be treated with hydrochloric acid, the iron disappears in combination with the acid, and sulphur is left. If, however, the compound of iron and sulphur be treated with the same acid the entire mass is attacked and disappears, not the iron alone, showing that the action now is between the acid and the compound as a whole.

CHAPTER V

HYDROGEN

Occurrence of Hydrogen.—Hydrogen is found free, that is in the uncombined condition, in but very small quantities. It is one of the substances composing the mixture called natural gas, and a trace of it exists in volcanic gases. It is produced to a slight extent in the decomposition of organic substances, and recently it has been detected in the atmosphere. It is, however, both plentiful and widely distributed in compounds. It forms one-ninth by weight of water, it is an important constituent of mineral oils, it enters into the composition of nearly all organic substances, and of many minerals.

Preparation of Hydrogen.—Hydrogen is generally prepared either from water or from hydrochloric or sulphuric acid. It is obtained from these either by the agency of the electric current or by the action of certain metals, such as zinc, magnesium or iron. Of these metals, some cause the gas to be set free from water at ordinary temperatures, while others act only at a red heat.

When a portion of acidified water is connected in an electric circuit and a current of sufficient strength passed through it, gases separate from it and collect at the ends of the metallic circuit. This is really a process of analysis, and is a common method of determining the composition of water, but incidentally it is an easy way of preparing small quantities of hydrogen.

When metallic sodium, potassium, or calcium is brought into contact with water, a very vigorous chemi-

cal action ensues, and hydrogen is set free. This is clearly shown when the metal is kept below the surface of the water as in Ex. 24; but when the metal floats the gas escapes, though exactly the same action goes on. The flame which often accompanies these chemical changes is produced mostly by the burning hydrogen, which is ignited by the heat energy developed. The characteristic colours of the flames are due to a little vapourised metal that passes off with the hydrogen. Sodium does not liberate all the hydrogen from water, but only half of it, because the other half can be subsequently obtained by proper treatment of the material that remains.

If steam, which is water in a convenient form for this experiment, be passed over red-hot magnesium, the metal burns to a white powder by combining with one of the elements composing the water, and the hydrogen thus freed from combination passes on, and may be collected. Hot iron acts on steam in a similar way, but does not glow. The magnesium and iron set free all the hydrogen from the water, so that only this gas and the solid substance formed with the metal remain.

The most convenient way to prepare hydrogen for laboratory use is to cause iron or zinc to act with either hydrochloric or sulphuric acid. Commonly zinc and sulphuric acid are the materials used; but in that case the acid should be diluted and heat should not be applied, for two reasons—(1) The compound formed when zinc acts with sulphuric acid is readily soluble in water, but is nearly insoluble in concentrated acid, so that the metal soon becomes coated with this compound, and is thus shielded from the acid; (2) Hydrogen set free in presence of hot or concentrated sulphuric acid is likely to act chemically with the acid instead of coming off as gas. This will be further explained under Sulphuric Acid.

Pure hydrogen may be obtained in small quantities either by decomposing water by the electric current, or by the action of pure metal on pure acid. The latter method cannot generally be employed because the substances are not easily obtainable, and sometimes, as in the case of zinc and sulphuric acid, they do not readily act together. The gas may be prepared in a convenient way and reasonably free from impurities by filling a vessel, such as a test tube, with water in which a little acid is mixed, inverting the vessel in a plate of water, and slipping pieces of magnesium under its mouth.

Properties of Hydrogen.—Hydrogen resembles air in appearance, as has been noted in the experiments. When prepared by electrolysis of water it is quite odourless, but when obtained from the action of metals with acids it often has a disagreeable odour due to other gaseous products formed from impurities in the materials which have been used. The combustibility of hydrogen and its relation to combustible substances are illustrated in Experiments 18-21. Hydrogen is the only element that produces water by combustion. It is true water is formed when substances like coal gas and acetylene burn, but this result is due to the hydrogen in their composition, so that it may be taken that the formation of water during combustion indicates the presence of hydrogen.

EXPERIMENT I. Balance accurately upon a scale a flask fitted with a solid rubber stopper, and having a capacity of about 300 c.c.'s. This may be readily done by placing a bottle and stopper on the other scale pan, and putting water into the bottle until the balance is in equilibrium; the final adjustment should be made with a pipette. Place the stopper in the bottle, which may then be left standing without loss through evaporation.

Remove the flask and invert it in a holder, take out the stopper and pass a stream of dried hydrogen upward into it until it is filled, then replace the stopper in the flask and put it back on the scale.

What does the balance show? What weight, in fractions of a gram, is needed to restore equilibrium? How much has the weight of the flask diminished? What does this weight measure?

Take the stopper out of the flask and lay it on the scale pan, then let the whole stand for five minutes.

What change occurs? To what is the gain in weight due? What conclusion does the experiment warrant? Measure the volume of the flask, and calculate how much heavier (in grams) a litre of air is than a litre of hydrogen. Given that a litre of air weighs 1.293 grams, what does a litre of hydrogen weigh? What is the sp. gr. of air, if hydrogen be taken as the standard ($H = 1$)?

If it were required to pour hydrogen from one vessel into another, how should these be held?

Hydrogen is the lightest substance known, one litre of it weighs .09 grams nearly, (.08987 to be accurate); while under like conditions an equal volume of air weighs 1.293 grams. On account of this property of lightness, hydrogen has been largely used for inflating balloons. A soap bubble or a toy balloon filled with the gas floats upward to the ceiling.

When liquefied, hydrogen vapourises at a temperature of -237° C., under a pressure of one atmosphere; that is, its boiling point in the air is -237° C.

The gas is very slightly soluble in water, as at 20° C.,—about the temperature of an ordinary living room—a litre of water dissolves 18.5 c.c. of hydrogen, or a little less than 2%.

Hydrogen burns with an intense heat. Thus the chemist expresses one fact connected with the properties of this gas by saying that two grams of hydrogen, in burning to water, set free 68,000 calories. This is another way of making the statement that the combustion of two grams of hydrogen gives off enough heat to raise 68 litres of water one degree in temperature. On account of the great amount of energy thus developed hydrogen is a very valuable agent in the industrial world, either when it is free or when it is in combinations that are easily decomposed. (Refer to the articles on the Oxhydrogen Flame, Coal Gas and Acetylene.)

Other properties of hydrogen will be referred to later, especially under the headings, Reduction, Hydrocarbons, and Hydrochloric Acid.

History.—In 1766 Cavendish, while experimenting with acids and metals, collected the gas given off and investigated its properties. He named it Inflammable Air, and discovered that when it burned water was formed. The present name of the gas was given to it by Lavoisier in 1783, and is derived from two Greek words that signify “water producer.”

Hydrogen was long classed as a “permanent gas,” that is, a gas which could not be changed into any other state; but in 1898, Dewar, an English chemist, succeeded in liquefying it by subjecting it to a temperature of -237° and a pressure of 180 atmospheres. This enormously low temperature was secured by allowing portions of the greatly condensed gas to suddenly expand, by escaping through a nozzle, a practical application of the “latent heat of expansion” (See Physics text-book). In 1900 Dewar further announced that hydrogen exists in the atmosphere in a free state, though in quantities so small as to be quite negligible under all ordinary circumstances.

PROBLEMS

1. Devise a method for determining whether hydrogen will diffuse sideways, or downward as well as upward.

2. Will hydrogen pass out of an open vessel that is turned mouth downward? How can the result of the experiment be explained in view of the fact that this gas is lighter than air?

3. Cast a plaster of paris sheet about one-eighth of an inch thick, between two plates of oiled glass, and cut it into three inch squares. Fill a gas jar with hydrogen and place it mouth downward over a similar jar standing mouth upward and full of air, but slip one of the plaster plates between the two jars. In half an hour test if there is hydrogen in the lower jar, and if there is air in the upper one.

4. Why were the names, Inflammable Air and Hydrogen, both appropriate for this gas?

5. Find, from an encyclopædia or a biographical dictionary, who Cavendish and Lavoisier were, when they lived, what noted work each did, and other particulars than those here given regarding the life of each.

6. A litre of hydrogen weighs .09 grams, a litre of air weighs 1.3 grams, approximately; how many grams would a cubic meter of hydrogen be capable of just lifting at standard temperature and pressure?

7. A flask of 337 c.c. capacity was fitted with a stopper and carefully balanced on a scale, dry hydrogen was passed into it until all air was displaced, then it was corked and replaced on the scale. Weights amounting to .406 grams had to be placed beside the flask to restore the balance. Knowing that 1 litre of air weighs 1.293 grams, find (1) the weight of hydrogen as compared with air; (2) the weight of one litre of hydrogen. Measure the capacity of a flask, and make the preceding calculations from original weighings.

CHAPTER VI

OXYGEN

Occurrence of Oxygen.—Oxygen is by far the most plentiful element, so far as the materials are known, that enter into the composition of the crust of the earth. It forms eight-ninths by weight of all water, and about forty-eight per cent. of the solid part of the globe, while it exists free in the air to the extent of 21% by volume, or 23% by weight. As it combines with nearly all the elements, its natural compounds are plentiful.

Preparation of Oxygen.—Although this gas exists in the air to a practically unlimited extent, there is no method by which small quantities of it may be easily and cheaply collected for laboratory purposes free from mixtures of other substances. When it is wanted for experimental use, therefore, it is usually prepared from some compound in which it exists, and which can be decomposed without difficulty. Water, mercuric oxide and potassium chlorate are such substances. In practice, the chlorate is commonly used, but it is found that when it is mixed with manganese dioxide, the gas is given off at a lower temperature than would otherwise be the case. (Refer to the article on Catalysis). Moreover, a little of this substance yields a large volume of oxygen, thus 122.6 grams—a trifle more than a quarter of a pound—gives off 33 litres of gas or 28 quarts, nearly.

Oxygen may be prepared from water by electrolysis, or by the agency of chlorine and red lead. (Experiment 85.)

It is also obtained from the air in two ways, when wanted in large quantities for industrial purposes. One of these is by the use of barium oxide, a substance very like lime, but with the power of taking up oxygen from the air when moderately heated under high pressure. When the heat is increased somewhat or the pressure reduced, the oxygen is given off and the oxide returns to its original condition. Barium oxide thus captures the oxygen and delivers it over for man's uses. The second method consists in liquefying the air and allowing it to vapourise again. The other ingredients mostly pass out first from this liquid, so that the last portion to evaporate is nearly all oxygen, and the gas is thus collected free enough from impurities to permit of its use.

Many other substances are known from which this gas can be prepared, but the methods are not of sufficient importance to receive consideration here.

Properties of Oxygen.—The chemical activity of oxygen, as shown by its numerous and easily produced compounds with other substances, is its most important property. Experiments 31-34 illustrate this characteristic, and show with what vigor this element enters into some of its combinations. In this connection it should be noted that as burning hydrogen forms water, the act of burning is chemically a combining with oxygen, so that the latter element in uniting with hydrogen produces water.

The solubility of oxygen may be found in the same way as that of hydrogen (Experiment 25). At 0° C. and a pressure of one atmosphere a litre of water will dissolve about 40 c.c.'s of oxygen, but at the temperature of an ordinary room about 25% less.

For other examples of the properties of oxygen, refer to the subjects: Oxidation, Hydrogen Dioxide, Nitric Acid, and Chlorine.

Uses of Oxygen.—Two purposes which oxygen serves stand out beyond all others; it is necessary for the support of life, and generally for combustion. There are cases in which burning may go on without oxygen, but these are rare, and of little consequence. Practically all life, both animal and vegetable, is dependent on oxygen, for if the supply of that gas be cut off, vitality ceases, except in the case of some lower forms of vegetable life. Aquatic animals must have oxygen, which they obtain from air dissolved in the water.

Apart from the uses of oxygen in supporting life, its most general application is in combining with fuels to furnish heat energy for domestic and industrial purposes. The heat in such cases results from a chemical union between oxygen and either carbon or a compound of carbon and hydrogen. There are, with unimportant exceptions, only two sources of energy available at present for such industrial needs as those of manufacturing, transportation and household operations. One of these has its origin in falling water, the other in the heat of combustion. But water is a compound of oxygen while combustion is the action occurring in the formation of some oxygen compounds. Man is therefore dependent on this element both for existence and for progress from the lowest savagery to his present stage of civilisation.

History.—Oxygen was discovered by Priestley in 1774; and about the same time Scheele, a Swedish chemist, also found it. Priestley, however, first published his results. His investigation has an interest for every beginner in chemistry, because the material from which he prepared the gas was red oxide of mercury, and his source of heat was the sun's rays converged by a burning glass. The name oxygen means "acid producer," and

was given to it by Lavoisier under the mistaken notion that the gas was a necessary constituent of all acids.

Oxygen was first liquefied in 1877; before that time it was classed as a permanent gas.

PROBLEMS

1. Weigh carefully one gram of powdered chlorate of potash, and after mixing it with manganese dioxide, put it in a hard glass tube, closed at one end. Place a loose plug of asbestos above the powder, and carefully weigh the whole. Heat the mixture and collect over water the gas that comes off. When the action is over let the tube cool, weigh it again and measure the gas.

What does the gas weigh? How much oxygen, by weight, could be got from 122.6 grams of chlorate? What would this oxygen measure in c.c.'s?

2. The names of Priestley and Scheele are connected with the early history of oxygen. Search for some particulars regarding the lives and achievements of these chemists.

3. What is burned hydrogen?

4. Water consists of hydrogen and oxygen, which are elements. Is water an element? Why?

5. Will a lighted splinter continue to burn in steam? Why? Will steam burn when brought into contact with a blazing splinter? Why?

6. Heat some brown oxide of lead in a tube and determine whether oxygen is given off or not.

CHAPTER VII

STUDY OF WATER

Repeat Experiment 2, so far as to observe the quantities of the gases set free at different stages of the process.

What are these gases? In what proportions are they set free?

It is clear from this experiment that water contains oxygen and hydrogen, but there is no conclusive proof that it is composed only of these substances; and, even if that were settled, it has not been shown that the proportions in which the gases have been set free are the same as those in which they combine, hence some further investigation is necessary in order to determine these points.

Experiments 38 and 39 illustrate the ways in which this may be done. The former, repeated many times, with precautions to avoid impure materials and to prevent loss, makes it quite clear that two volumes of hydrogen unite chemically with one volume of oxygen to form water.

When Experiment 39 is carried out with such precautions that only pure hydrogen is used and that no water vapour escapes, the proportions by weight in which the gases unite is found to be *one* of hydrogen to *eight* of oxygen, thus the composition of water is, by weight, eight-ninths oxygen and one-ninth hydrogen.

Uses of Water.—Water is the most general solvent known; not only in its pure state, but very often when substances are dissolved in it, these solutions become effective solvents for materials that are scarcely affected

by water alone. Thus if a saturated solution of iodine be made with solid iodine still in the vessel, and a crystal of potassium iodide be dropped into it, the change in colour will indicate a much greater solubility of the iodine in the solution of potassium iodide than in pure water. Many of the changes in the earth's crust are dependent on chemical or physical actions somewhat similar to this. For instance, mineral veins have been filled with ores deposited from solution. Quartz, or silica, has been extensively dissolved by hot alkaline waters under pressure; and limestones are constantly being dissolved by water that has previously become a solution of carbon dioxide.

Water is necessary for both plant and animal life, hence its importance in agriculture, and the endeavour to make up by irrigation for the lack of precipitation in those regions that for physical reasons have little rainfall. The facts that water is not combustible, and that it changes from the solid form through the liquid state to a gas within a small range of temperature (one hundred degrees Centigrade), render it a very valuable agent for making the chemical energy of oxygen and coal available for mechanical purposes.

Recently chemists' investigations have shown that water, as gas, plays a part formerly unsuspected in producing combinations. Thus perfectly dried hydrogen and oxygen cannot be made to unite, but if a trace of water vapour be introduced into the mixture they combine at the temperature of a blazing match. Phosphorus, too, one of the most combustible of substances under ordinary conditions, may be vapourised in perfectly dry oxygen without combining with it, but a trace of water gas causes the union to take place at once.

Such illustrations make it clear that the chemistry of a perfectly dry world would be vastly different from that

of the one we know, where water covers a large part of the surface; and, either as liquid, vapour or gas, is present practically everywhere in air and soil.

All waters that occur naturally are contaminated with dissolved impurities from the air or earth. Pure water can be secured by distilling that obtained from springs, rivers, lakes, etc. The process of distillation consists in vapourising the water and condensing the steam. In this operation, by rejecting the first and last parts of the distillate, *i.e.*, the condensed liquid,—both the gaseous and solid impurities may be largely eliminated.

CHAPTER VIII

STUDY OF AIR

The experiments dealing with the composition of air show that it is made up of at least two substances, one of which may be removed by causing it to combine with hydrogen, phosphorus, copper or other such substances. This constituent of the air is evidently oxygen, because it forms the same compounds with the elements just mentioned that pure oxygen did, only the action is less vigorous.

The gas that remains after oxygen is removed from air is mostly nitrogen. There is, however, usually mixed with it some water vapour and carbon dioxide (page 118) as well as a very small quantity of hydrogen and of the rare gases argon and helium. For all practical purposes, air may be considered to be a mixture of oxygen and nitrogen in the proportions of 21% of the former and 79% of the latter by volume (the exact quantities are 20.8 and 79.2 per cent.).

The presence of water vapour in the air is demonstrated by the use of apparatus like that of figure 1.

The U tube is filled with lumps of caustic soda or of fused calcium chloride, and the increase in the weight of the tube is a measure of the amount of moisture in the

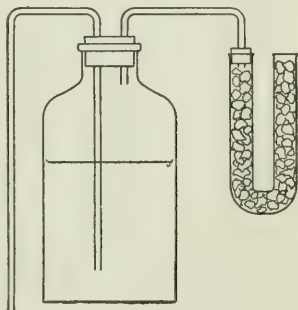


FIG. 1

air that passed over to take the place of the water siphoned off.

The siphon may be replaced by a funnel tube, and the U tube by a bottle containing lime water; then if the large bottle be filled with air and water slowly poured down the funnel tube, the air will be driven through the lime water; if the latter turns white (milky) that indicates the presence of carbon dioxide. It may require several bottlefuls of air to give a perceptible result.

Air is a mixture of oxygen and nitrogen, not a compound of these gases. In confirmation of this statement the following facts may be noted:

(1) When oxygen and nitrogen are brought together in proper proportions a substance is formed which cannot be distinguished from air, but there is no transference of energy that can be detected except that spent in bringing the substances into contact with each other, though such change of energy is a part of every chemical action.

(2) Oxygen and nitrogen are not present in the air in the proportions in which they enter into combination. Several compounds of these gases are known, and in all of them there are sixteen parts, by weight, of oxygen to fourteen of nitrogen, or simple multiples of these weights, but in air the quantities are not related as sixteen and fourteen, or any simple multiple of these numbers.

(3) Air does not go into solution or enter into combination as a single substance, or as one kind of matter, but each constituent acts quite independently of the others. For instance, when air is dissolved, the quantities of oxygen and nitrogen in the solution are not in the proportions existing in the atmosphere, but what happens is exactly what would take place if these gases were mixed in the proportions found in the air and subjected to a pressure of one atmosphere, over water. About one-

fifth as much oxygen and four-fifths as much nitrogen dissolve as would do so if each gas existed alone. (See Dalton's Law of Partial Pressures in some text-book on Physics).

(4) Air can be liquefied, but when the liquid vapourises it does not do so as one substance. The nitrogen is more volatile than the oxygen, hence the first part of the gas that passes off contains more nitrogen and the last part more oxygen than air does. This would be impossible in the case of a compound; water, for instance, evaporates as water, not as hydrogen and oxygen.

The supply of oxygen required for the support of plant and animal life (page 24) is all obtained from air. In the case of warm-blooded animals, bodily heat is derived from chemical action between oxygen and waste matters of the system. The part that nitrogen plays in the growth of plants will be referred to under that gas.

Air is necessary in the burning of fuels for light and heat. Everyone knows the need of a good draft to increase combustion, and the certainty that a fire will die out if the supply of air is shut off. The atmosphere, too, is the agency by which moisture is distributed to those regions distant from bodies of water, and this circulation is a necessary condition of the earth's productiveness. Finally, the shell of air about the earth with its clouds and vapour hinders rapid loss of the heat into which the radiant energy of the sun is changed at the earth's surface, so that the temperatures of the day and night are somewhat equalised.

CHAPTER IX

CONSERVATION OF MASS

Experiments 43-45 illustrate the way in which investigations have been carried out to determine if there is either gain or loss of matter in chemical actions. In the first example two colourless liquids produce a solid substance, but the entire mass remains unchanged so far as the quantity of matter is concerned, because the weight is unchanged and weight is the measure of mass. In the second case, the phosphorus disappeared, a dense white vapour was produced, but the weight was not altered, so that the quantity of matter was constant throughout. In the third experiment the piece of stone ceased to exist, but the matter composing it did not. There was no substance present at the end of the experiment that had the essential properties of marble or calcite, but the substances of which the piece of

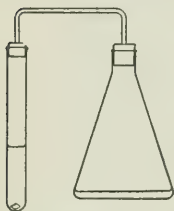


FIG. 2

rock was composed were not destroyed, they simply formed other compounds. The liquid in the flask was chosen because the gas set free in the test tube combines with it very readily, thus no matter escaped during the operation.

These three experiments do not establish a law; they only illustrate a method of investigation. Many experiments similar to these have been carried out with great care and they all lead to the one conclusion, that in chemical actions *matter is neither made nor destroyed*; it may be

detached from its former compounds, may appear in new forms, may enter into fresh combinations, but it exists in the same quantity by weight at the end that it did at the beginning of the process. This principle is referred to as the **Law of Constant Mass**. *Law here is used in the sense that all experience in dealing with matter leads to this conclusion, and no fact is known which is in contradiction of the principle.*

Law.—The mass of the substances taking part in any chemical action is constant.

CHAPTER X

OXIDATION AND REDUCTION

When oxygen unites chemically with another element the compound formed is an *oxide* of that element, and the process of union is called **Oxidation**. Thus, water is an oxide of hydrogen, as shown in Experiment 37. An oxide of phosphorus was produced in Experiment 32, and again in Experiment 41. Experiment 6 illustrated the oxidation of copper, and in 8 magnesium was oxidised. When oxidation is accompanied by light and heat, as in Experiment 32, it is classed as *combustion*. The chemical actions were similar in Experiments 32 and 41; the products, both of matter and energy, were alike in quantity, yet the vigour of the combination in the former case caused the energy to be quickly liberated, and it thus affected the senses as light and heat. When a substance loses all, or part, of the oxygen it contained, it is said to become **Reduced** or **Deoxidised**. Thus in Experiment 4 the oxide of mercury was reduced to metallic mercury simply by heating. Experiment 6 illustrates both oxidation and reduction, the latter by the combined influence of heat and coal gas, or of heat and charcoal. Experiment 27 is an example of both kinds of action, as is also Experiment 46. In the former the oxide of hydrogen (steam) became reduced to hydrogen, while the magnesium combined with the oxygen thus supplied and became altered to the oxide of magnesium. In Experiment 46 the process was reversed, for the oxide of iron was reduced to the metal while the hydrogen was

oxidised to water. For practice in this connection it will be well to study the oxidations and reductions that occurred in the following experiments: Nos. 1, 6, 8, 27, 28, 31, 32, 37 and 41.

Oxidation is one of the processes of decay in nature. Not only organic materials, but substances of mineral composition, are subject to its action. The oxygen and moisture of the air are, in part at least, the agents by which animal and vegetable matters rot away mostly to gaseous materials, and rocks disintegrate to sands and clays. The burning of fuels and the rusting of exposed metals are actions due to oxidation. It is, too, a common laboratory process in chemical operations, of which examples will frequently occur in the following pages. It is often more practicable to employ substances rich in oxygen for this purpose than to use the free element. Thus yellow lead oxide in water is not affected by passing oxygen gas through it, but if it be boiled with nitric acid it turns to a dark brown colour, and is altered into another oxide containing twice as great a proportion of oxygen as the yellow compound does. Substances which thus supply oxygen to others to produce oxidation are known as oxidising agents. Some common ones are nitric acid, chlorine, the peroxides, nitrates, chlorates and permanganates.

Among the oxides water naturally takes first place, both on account of its quantity and uses; but many valuable minerals and ores must also be placed in this class, as hematite and magnetite, ores of iron; corundum and emery, oxides of aluminium; cassiterite, an oxide of tin; the varieties of quartz, oxide of silicon; and pyrolusite, the common ore of manganese. Some oxides of industrial importance are those of calcium, known as lime; of carbon, used in soda water manufacture; of arsenic, employed

as an insecticide; and of sulphur, from which sulphuric acid is made.

When there is more than one oxide of a substance, the oxidation may take place in successive stages. This may be illustrated as follows: If some red lead be heated in a hard glass tube it will yield oxygen, and become reduced to a yellow powder, which is still an oxide of lead, because when heated with charcoal or hydrogen it will be reduced to metallic lead. If, now, some of this yellow oxide of lead be boiled with nitric acid, it turns brown, and the brown powder, when dried and heated, yields oxygen and returns to the yellow powder that was treated with the acid. Lead heated in oxygen gives the yellow oxide, this treated with nitric acid yields the brown oxide, and the latter, on heating, parts with some of its oxygen to again form the yellow oxide, but this heated with hydrogen or carbon becomes reduced to metallic lead, hence both oxidation and reduction may occur in stages.

Reduction is chemically important because it is the process of *smelting* by which ores are changed into metals. The problem in such cases is to remove the element or group of elements with which the metal is combined. For instance, in the reduction of hematite (one of the most valuable of iron ores and chemically an oxide of iron), the operation consists in causing the oxygen to combine with carbon, thus leaving the iron free. (Refer to this subject under Carbon.)

PROBLEMS

1. Air is 23% oxygen by weight, and water vapour is 89% oxygen. Why then does a splinter that is burning freely in air not burn when held in water vapour? Magnesium which burns in air also burns in steam when made red hot, how is this action accounted for?

2. Should oxidation be classed as a physical or as a chemical change? Why?

3. If a piece of stove pipe iron were exposed to the action of moist air until only a brownish brittle mass remained, how would the weight be affected? Why?

4. Apart from ornamentation, what purpose is served in painting exposed woodwork and ironwork? Soldiers rub oil on their gun barrels to keep them bright; how does the oil protect the iron from rust?

5. The utensils for domestic use are made of steel sheets coated with tin. The latter metal is soft and wears away with use. What then happens to the iron? What purpose does the tin serve? Is copper affected by the air to any considerable extent? (Examine a copper telephone wire that has been up several months.) Mention several metals that rust only slightly or not at all in air, and some uses to which they are put on this account.

CHAPTER XI

STUDY OF SULPHUR

The yellow solid known as sulphur may be distilled, that is vapourised, and the vapour condensed (Experiment 47); when this is done the resulting substance is known as Flowers of Sulphur; but if melted sulphur is run into moulds and allowed to cool, it forms Roll Sulphur. If either kind be raised to boiling temperature, then poured into cold water, there results Plastic Sulphur.

It is clear that this last form differs very greatly from the other two, yet they are chemically the same substance because they form the same compounds with other elements when treated in the same way, with oxygen for instance. (Some elements exist in forms that appear to be entirely different substances, though chemically they are identical) These are said to be *allotropic forms* and the property of existing in this way is known as *allotropism* or *allotropy*. These terms do not apply to different states (solid, liquid and gaseous) of the same substance. (For further discussion of allotropism see page 110). The two kinds of yellow sulphur are not allotropic forms, because the difference here is due to condensation only; it is an exact parallel of water in the forms of snow and ice.

Oxides of Sulphur.—When sulphur burns in air it forms a gaseous oxide that is soluble, has a sour taste, does not burn, and turns moist litmus red.

As in the case of oxygen and hydrogen, it is not difficult to determine the proportions in which sulphur and

oxygen combine. Thus, if a weighed quantity of sulphur be put into a tube and heated in a current of oxygen, combination accompanied by light and heat takes place, that is, the sulphur burns; and if the gaseous product be passed through a weighed U tube containing caustic soda, it will be intercepted, and the quantity of oxide produced by the sulphur can be found from the increase in weight of the soda solution.

Since chemical action takes place between quantities by weight of matter it follows that there must be in every case a certain smallest quantity—a unit mass—that takes part in such action. This unit mass must have weight and must occupy space. For convenience it is called the *combining weight* of the substance. For instance, when water is decomposed by the action of the electric current the quantities of the gases set free become gradually greater, that is, they increase by additions of new portions of the same kind of matter, and the smallest possible addition that could occur is one combining weight of oxygen in one case, and of hydrogen in the other. As a matter of fact, it consists of one combining weight of oxygen with two of hydrogen.

When sulphur burns in air or in oxygen, one combining weight of sulphur unites with two of oxygen to form the gaseous oxide already mentioned; and sulphur does not combine *directly* with oxygen to form any other oxide. These two substances are, however, found combined in other proportions, for this oxide may be made to undergo further oxidation by special treatment.

EXPERIMENT II. Twist some fibres of asbestos into a knot, soak this in platinic chloride, then hold it in a gas flame until it glows for some time. A grey deposit on the fibre indicates metallic platinum. Carefully pass this fibre with its load of metal into a hard glass tube

open at both ends, heat the asbestos to redness, then pass slowly through the tube a mixture previously prepared of two volumes of oxide of sulphur (see Experiment 49), and one volume of oxygen. Slip a dry, clean flask over the outlet of the tube.

Is there any indication of chemical change? Shake a few drops of water into the flask, then test with barium chloride. A white precipitate indicates the presence of sulphuric acid. What combination could have occurred? Is this a case of oxidation? How many oxides of sulphur have been made in these experiments?

There are two matters of importance connected with this experiment; the first is that, in some cases, the higher oxidation product of an element may be formed by stages; that is, a lower oxide may be changed to a higher one by proper treatment. The second is that chemical actions may at times be brought about by the presence of substances that do not themselves undergo any chemical change. The material on the asbestos fibre was platinum at the beginning of the operation, and was platinum at its end; the asbestos served simply as a frame on which to suspend the metal. The point to be noted in this connection is that the lower oxide of sulphur and oxygen combine in presence of red-hot platinum, though they will not unite by simply heating them together, and the metal is not in any way altered during the process. This subject will be dealt with more fully under the head of Catalysis.

Both oxides of sulphur when dissolved in water form solutions that are sour to the taste and turn blue litmus red, and these are two common characteristics of a class of compounds called *acids*, so that the further conclu-

sion may be drawn that *oxides of sulphur in solution form acids*.

A compound of sulphur with another element is named a sulphide of that element; thus, hydrogen and sulphur in combination form a sulphide of hydrogen. This compound is made up of two combining weights of hydrogen united with one of sulphur; therefore, in composition, it is similar to the oxide of hydrogen; indeed, it may be looked upon as water in which the oxygen is replaced by sulphur. The oxide of hydrogen is easily obtained by heating a mixture of the two gases, but the sulphide is not readily prepared in this way, though it may be formed when sulphur vapour and hydrogen are heated together at a high temperature out of contact with air.

The preparation of the gas from iron sulphide and hydrochloric acid resembles many chemical actions in that it consists of a rearrangement of the elements composing the original substances. Iron sulphide is made up of iron and sulphur, and hydrochloric acid is a compound of hydrogen and chlorine; when these two are put together their constituents change partners, the iron uniting with the chlorine and hydrogen with the sulphur. As the latter substance is a gas it quickly saturates the solution, then passes off from the liquid.

Hydrogen sulphide in water solution is a weak acid which has the property of forming sulphides of most of the metals when passed into solutions of metallic compounds.

Hydrogen sulphide occurs in nature in the waters of many mineral springs, in volcanic gases, and in the decomposition of organic substances, especially those rich in albumen. It is formed in the distillation of coal, and is one of the impurities of illuminating gas that have to be removed before the gas is fit for use. Gas escaping

from a furnace or stove burning coal contains this substance, and that is the reason that silverware exposed to furnace fumes turns black. Compare Experiment 50. The "oxidised" silver of commerce is really "sulphidised" silver, due to the action of hydrogen sulphide on the silver.

Sulphuretted hydrogen is another name for this gas.

(Sulphuric Acid will be taken up in Chap. XLIV.)

NOTES ON SULPHUR

Sulphur occurs free—that is, not combined with other elements, though mixed with impurities—mainly in regions of volcanic activity. As it vapourises readily, large quantities appear to be carried out of the craters as gas and condensed in the cool air. In other places there are deposits that seem to have been formed by the decomposition of rocks or minerals that were rich in sulphur.

Many valuable ores are sulphides of metals. For example, galena is sulphide of lead, zinc blende is a sulphide, pyrite is a sulphide of iron worked mainly for its sulphur content, arsenopyrite (mispickel) is a compound of arsenic, sulphur, and iron; argentite is the sulphide of silver, and cinnabar is a sulphide of mercury.

Until quite recently the Italian volcanoes have supplied the sulphur market of the world, but a very large deposit of this element in the bedded rocks of Louisiana is now yielding enough to supply the requirements of this continent. Holes are drilled some 700 feet through the overlying rocks, pipes are passed down and superheated steam driven through them; the steam at 300° C. melts the sulphur, which is pumped to the surface and cooled.

The world's manufacturing industries use about half a million tons of sulphur yearly, most of which goes to make sulphuric acid.

Iron pyrites, or pyrite, is a common mineral in the rocks of Northern and Eastern Ontario. It is a sulphide of iron that is 53 per cent. sulphur, and when broken up and roasted in a current of air, a large part of this sulphur is obtained as the same oxide that is produced by burning sulphur, so that it is thus available for the manufacture of sulphuric acid.

CHAPTER XII

SODIUM

Sodium is a beautiful silver-white metal that almost instantly tarnishes when exposed to the air because it rapidly oxidises. For this reason it can be preserved only when out of contact with air or other substances that readily yield oxygen. Generally it is kept covered with coal oil because that liquid is composed of carbon and hydrogen only. The untarnished metal may be kept permanently by sealing it up in an atmosphere of hydrogen. If a tube be drawn out, as in the diagram,

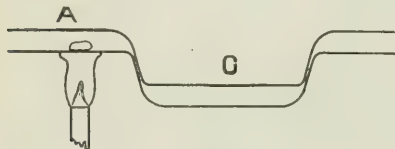


FIG. 3

and clean sodium put in it at A, while a current of hydrogen is passing through, the metal when heated will melt and run down into the part C, which must also be kept

hot to prevent cracking; finally the tube may be sealed off at the narrow parts and allowed to cool. Sodium belongs to the class of elements called metals. These are distinguished from the non-metals by their appearance (lustre), by their properties of freely conducting heat and electricity, by forming certain compounds, especially hydroxides, and by replacing hydrogen in acids. This metal is one of those that decompose water at ordinary temperature, Experiment 24, and in so doing it sets free a large quantity of heat energy. An interesting variation of the experiment with sodium and water is to

drop a small piece of the metal on ice; indeed the amount of heat developed can be approximately calculated from the quantity of water formed.

Secure two blocks of ice with smooth plane surfaces, make a cavity in one and drop a piece of sodium of known weight into it. Then quickly cover it with the other block. When the action ceases, measure the water as accurately as possible; and from the latent heat of fusion of ice, calculate how many heat units would be set free by a gram of sodium acting on ice, or on water, for the chemical actions are identical.

Only half the hydrogen contained in the water is set free by sodium; the compound that the metal forms with the remaining hydrogen and oxygen dissolves in the excess of water, and imparts to it those properties which cause sodium to be classed as an alkaline metal.

When an alkaline substance is added gradually to an acid, each slowly loses its characteristic properties until a stage is reached at which the mixed solution is neither acidic nor alkaline. It is then said to be *neutral*, and the process of bringing it to that condition is known as *neutralising* one substance with the other, though the chemical action is mutual.

Sodium in union with chlorine forms common salt, (Experiment 56), and when sodium hydroxide and hydrochloric acid neutralise each other, the chemical action results in an interchange of elements. Thus hydrochloric acid is composed of hydrogen and chlorine, while sodium hydroxide has for components sodium and hydroxyl (see page 61). The new arrangement leads to a union of the sodium and chlorine on the one hand, and of hydrogen and hydroxyl on the other. Salt, which occurs plentifully in nature, is the source from which sodium is obtained. The method of its preparation and the chem-

istry of its compounds cannot be taken up until some further knowledge of general principles has been acquired. For the present it is sufficient to know that sodium is an alkaline metal which combines readily with water, setting hydrogen free; and that it neutralises acids, forming new compounds in the process.

CHAPTER XIII

ACIDS, BASES, AND SALTS

Mention has been made on several occasions of acids, and acid-forming substances; it will be well, therefore, to learn something of the properties that distinguish them from other kinds of matter.

If a drop of sulphuric acid be mixed with twenty drops of water the liquid may be tasted by touching to the tongue a pencil or glass rod wet with the mixture. It may also be tested with litmus. If a little sulphuric acid be poured into a dish and a pair of electrodes (Fig. 4) dipped into it, as soon as the current is turned on an electrolytic action will begin and hydrogen will be set free at the cathode. If some dilute sulphuric acid be slowly dropped into a solution of sodium hydroxide, both the acid and alkali will lose their characteristic properties, and if the neutral solution be evaporated to dryness a white solid will remain. It has been found, too, that if a metal like zinc or magnesium or iron be placed in dilute sulphuric acid, a chemical action will ensue, both metal and acid will gradually disappear as metal and acid, while new substances will be formed, one of which will be hydrogen.

These changes are not peculiar to sulphuric acid; it has been chosen as a typical member of the class of acids; and the properties illustrated in the operations just described characterise acids as a group of substances. It must not be assumed that the reactions in all cases are so marked as they are when sulphuric acid is used,

but they are similar in character though varying in intensity.

Acids are all compounds; they have hydrogen as one component; they turn blue litmus red in varying degrees, they are mostly sour to the taste, they may be decomposed electrolytically, and hydrogen is then set free at the cathode. Metals, with few exceptions, will displace hydrogen from acids and will form new compounds with the part of the acid that remains after the hydrogen is liberated. All acids may be neutralised by alkalies.

When the hydrogen of an acid, either in whole or in part, is set free by the action of a metal, something more than the mere liberation of the gas occurs; the metal takes the place of the hydrogen in the compound, hence the new substance formed differs from the acid by having a portion of metal as one component instead of all, or part, of the hydrogen that was in the acid. The hydrogen of an acid that may be thus replaced by a metal is called *replaceable hydrogen*, and the new compound that is produced by the replacement is called a *salt*. An acid and its salt differ in their composition in only one respect, the acid is composed of a definite quantity of hydrogen in union with *a fixed portion of one or more other elements*; the salt derived from that acid consists of a definite quantity of metal in union with the *same fixed portion of the same one or more other elements*.

A **salt** may be produced by the action of a metal (with a few exceptions) on an acid; hydrogen is then set free. Zinc and sulphuric acid furnish an illustration. In some cases, as that of nitric acid and zinc, the hydrogen does not come off as free gas, but combines with some other substance present; hence zinc and nitric acid cannot be used for the preparation of hydrogen gas. (See under Nitric Acid). A salt may also be formed by the action

of a metallic oxide or of a hydroxide on an acid. Hydrochloric acid with copper oxide, and sulphuric acid with sodium hydroxide, are examples. The salts in these cases are precisely the same as those produced when the metal of the oxide or of the hydroxide acts with the acid; but the hydrogen instead of escaping as free gas enters into combination with the oxygen or hydroxyl. So far as the salt is concerned it is quite immaterial whether copper, copper oxide or copper hydroxide be treated with hydrochloric acid. The other substance resulting from the action will be hydrogen when the metal is used, oxide of hydrogen (water) when the oxide of the metal is acted on, hydroxide of hydrogen (also water) when the hydroxide of the metal is employed.

Base is a rather unsatisfactory term as used in chemistry, because of the various meanings that have been given to it. Formerly it was applied to that portion of a salt which remained when the volatile part was driven off by heating; these residues were oxides, so bases were defined as metallic oxides. Recently the term has come to be applied to hydroxides only, and a hydroxide is a compound of a metal with hydroxyl, the latter substance being composed of one combining weight each of hydrogen and oxygen. The reason why the name base is given to hydroxides, cannot well be discussed until the subject of ions and ionisation has been taken up, then it will be possible to give both acids and bases a little fuller consideration. (Compare page 67),

CHAPTER XIV

LAW OF DEFINITE PROPORTIONS

When studying the composition of water the experiments illustrate a very remarkable phenomenon, viz., that the elements enter into the union only in fixed proportions; by volume, two of hydrogen to one of oxygen; by weight, one of hydrogen to eight of oxygen. The experiments on the neutralisation of acids and alkalies show that a fixed weight of alkali requires a proportional weight of acid to unite with it. Similarly, potassium chlorate always loses a fixed percentage of its weight when strongly heated, and the weight of the substance formed when sodium is thrown upon water and the whole evaporated to dryness is an unvarying multiple of the weight of sodium taken. Copper oxide loses a constant percentage of its weight when heated in coal gas, and the copper dust that remains gains a fixed percentage if heated in air. All investigation regarding this matter has led to but one conclusion, that chemical action takes place between fixed quantities by weight of the reacting substances, and only between fixed quantities. Water, for instance, is eight-ninths of its weight oxygen, and if hydrogen and oxygen combine in any other proportions the result will not be water, but some other substance.

These chemical facts are expressed as the **Law of Definite Proportions**, in such words as these: *A compound always consists of the same constituents in the same proportions by weight.* The reason for the belief in the univer-

salinity of this principle rests on a great number of investigations in which it has been found to hold true, and upon the absence of any well-defined case contradictory of it. The term law, as here used, is simply the statement of a general principle.

CHAPTER XV

THE ATOMIC THEORY

Naturally those interested in chemical study were anxious to find some satisfactory explanation for the striking facts enumerated in the Law of Definite Proportions. Closely allied to this principle was another equally important one, viz., if two elements unite to form more than one compound with each other, a fixed quantity by weight of one of them unites with portions of the other which are simple multiples, by weight, of the smallest part of that other that enters into any combination. (Simple multiple here means a small integral multiple, as two, three, four, or five.) This is known as the *Law of Multiple Proportions*, and will be referred to more fully under carbon and its compounds. The problem confronting the early chemists, then, was to find answers to the two following questions: (1) Why does one element combine with another in only fixed proportions? For example, seven parts, by weight, of iron unite with four of sulphur, and if there be excess of either substance, that excess will remain unchanged. The experiments with hydrogen and oxygen, zinc and sulphuric acid, sodium hydroxide and acid solution, are examples of this law that have been met with at the very beginning of chemical study, and *there is no exception known to the rule, as it has been stated.* (2) Why do the elements combine only in proportions that are integral multiples of the smallest weights of them that enter into any combination? Thus hydrogen and

oxygen combine as two to sixteen in water, and as two to thirty-two in another compound. Sulphur unites with oxygen in proportion of thirty-two to thirty-two (twice sixteen) in one case, and as thirty-two to forty-eight (three times sixteen) in another. Two hundred parts of mercury form one combination with thirty-five and a half parts of chlorine, and another one with seventy-one parts of the same element. A large number of such examples might be cited, but they all come under the principle just stated.

To account for these and similar phenomena, **The Atomic Theory** was propounded. This assumed that in the division of elements into smaller and smaller portions there would finally be a condition in which the parts would be so small that no further division would be possible. These ultimate units of matter were supposed to have the form of minute particles, and to be also the units that take part in chemical action. For instance, if an element were set free, as hydrogen from sulphuric acid, it was displaced as these minute unit portions; and in combinations such as in the formation of water two particles of hydrogen uniting with one of oxygen composed the smallest part possible of the new substance. These final subdivisions of matter were named **Atoms**, meaning indivisible parts.

This theory of atoms being small, indivisible particles of matter, has now to be abandoned, for modern investigation has shown that the *atom*, as the term was formerly used, is a very complex structure, made up of yet more minute parts. Still *the unit masses of the elements taking part in chemical actions have not changed*, and it is convenient to retain the old terminology, but modified in meaning. Further, this use of the term atom does not, in any way, serve as an explanation of the chemical facts mentioned

above; it is simply a ready way of expressing a theory regarding them. For instance, if water in the form of gas be continually divided into smaller parts, a stage will finally be reached when further division will yield not two portions of water, but oxygen and hydrogen. This smallest mass of water consists of two unit masses of hydrogen united with one of oxygen. Notice, it is not said two *particles* of hydrogen and one of oxygen, but two *units of mass* which may consist of a great number of smaller parts. Since mass is measured by weight these units may be referred to as *combining weights* of hydrogen and of oxygen, but it is more desirable on the whole to keep to the former nomenclature with the somewhat restricted meaning given above.

An **Atom**, then, will be taken as signifying the Unit Mass of an element that takes part in chemical reactions. This does not in the slightest explain why there are unit masses of definite weights; it simply states that nothing less than this unit ever enters into combination or is displaced from a compound. According to this, atoms of the same element are always uniform in mass and alike in properties, but atoms of different elements vary in mass and in properties. The smallest proportions in which the elements combine with one another, then, represent the relative masses of their atoms, or the units of combining weight.

If an element be set free from combination it is by separation of successive atoms from the compound, but it does not follow at all that these atoms remain as individual objects; in fact, there is very good reason for believing that they sometimes arrange themselves in groups of two or more units each (see page 131.)

When a group of atoms combines, the united mass is called a *molecule*, whether it be made up of one element

or more than one; thus a molecule of hydrogen consists of two unit masses (atoms) of that element united in a single group, while a molecule of water consists of three atoms, two of hydrogen and one of oxygen, not as three separate things, but as three parts of one whole group. A molecule is, therefore, the smallest part of a substance which exists in a free state, for, if the molecule be divided, it is no longer the same substance but its constituents.

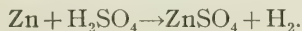
CHAPTER XVI

CHEMICAL SYMBOLS AND FORMULÆ

For convenience in representing chemical actions, a system of symbols has been devised. Each of these symbols represents a unit mass, one atom, of the element for which it stands, thus H stands for one atom of hydrogen, 2N for two atoms of nitrogen, and 4C for four atoms of carbon. A group of symbols without connecting signs constitutes a formula, and it signifies that the substances represented by the symbols have formed a compound. H_2O denotes that two atoms of hydrogen and one of oxygen have combined to form a molecule of water. C_2H_2 (read C two, H two) means that two atoms of hydrogen and two of carbon have united to form a molecule of a compound, in this case, acetylene. Symbols or formulæ connected by a plus sign indicate that the substances are mixed, or in contact, but not chemically combined. Symbols written side by side without any connecting sign mean that the elements represented have combined, thus $\text{H} + \text{Cl}$ means a unit mass, or one atom of hydrogen and a unit mass, or one atom of chlorine, in such a position that they can react chemically; but HCl stands for one molecule of a new substance, formed by the union of the unit masses of hydrogen and chlorine represented by the previous notation. CaCO_3 stands for a molecule consisting of five atoms of three different substances. The symbol standing alone means one unit mass of the element, with a numeral before it, as 2H; 3O, the quantity of matter, is that multiple of the unit mass, but

existing separately as individual atoms. A number written below and to the right also indicates that many atoms, but united to form a molecule or part of one, as H_2 , O_3 , S_8 , $\text{Ca}(\text{HO})_2$, $\text{Cu}(\text{NO}_3)_2$, Na_2HPO_3 .

The sign of equality (=) or an arrow head (\rightarrow) occurring in a group of chemical formulæ is to be translated into the word yields, or gives, or produces, or forms.



means that one combining weight, or atom, of zinc in connection with one combining weight or molecule of sulphuric acid forms one molecule of a compound called zinc sulphate, and one molecule of hydrogen, the latter consisting of two atoms of the same kind of matter in union.

This equation also expresses the numerical relationship of the weights of the substances. Thus 65 parts by weight of zinc react with 98 of sulphuric acid to form 161 parts of zinc sulphate and 2 of hydrogen. This statement is true for any unit of weight whatever.

$\text{NH}_4\text{HO} \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$ expresses the fact that ammonium hydroxide, NH_4HO , will form ammonia, NH_3 , and water under suitable conditions, but that ammonia and water will change back to the hydroxide when circumstances favour that action. In other words, such accompanying conditions as temperature, pressure and degree of concentration will, in part, determine whether the reaction will go in the direction of decomposing the single compound into its constituents or of reuniting these separated substances again.

The word *reaction* is often used to express that rearrangement of matter or regrouping of atoms that occurs when substances act together chemically.

A chemical equation is a brief way of indicating the substances that enter into a reaction and those that emerge from it, or an equation is an expression, by means of the recognised notation, of the first and final materials of a reaction. It also expresses the fact that the total mass of reacting substances is equal to the total mass of the products. It does not, however, express any intermediate changes that may occur, nor does it indicate transference of energy, neither does it show what treatment has been adopted in order to produce the result. Symbols, formulæ, and equations represent only substances and interchanges of matter. From the Law of Conservation of Mass, it will be clear that no matter can be either gained or lost during a reaction, therefore every atom that appears on one side of an equation must be accounted for on the other, though perhaps in a different group. Equations, too, indicate changes in molecular composition, therefore they deal only with atoms and molecules.

(an atom) of an element is the number
that expresses the ~~number~~ how many
times its atom is heavier than an
atom of hydrogen.

CHAPTER XVII

ATOMIC WEIGHTS

Two volumes of hydrogen combine with one of oxygen to form water; but, by weight, hydrogen unites with oxygen in proportion of one to eight, nearly; hence one volume of oxygen weighs approximately eight times as much as two volumes of hydrogen; or a unit combining mass of oxygen is sixteen times as heavy as the hydrogen unit.

The ratios of weights of unit masses or atoms of the elements, are called *atomic weights*, and are referred to oxygen, whose weight is assumed to be 16. The table on next page contains the names, the symbols, and the atomic weights of some of the more common elements; the weights are referred to oxygen as 16, and are only approximate in some cases. A complete table will be found on page 185. In it the atomic weights are expressed with accuracy. Formerly hydrogen was taken as the unit, then oxygen had the value 15.88. For convenience, chemists agreed on the International table of atomic weights on the basis of oxygen being called 16. Hydrogen then becomes 1.01, (1.008 accurately).

Heat energy set free, or absorbed, is sometimes expressed by the number of calories written after the symbols of reactions; thus

$\text{H}_2 + \text{Cl}_2 = 2\text{HCl} + 44000 \text{ Cal.}$, and conversely

$2\text{HCl} = \text{H}_2 + \text{Cl}_2 - 44000 \text{ Cal.}$ The first expression signifies that two grams of hydrogen and 71 grams of chlorine when subjected to proper treatment unite, and, in doing

NAME	SYMBOL	AT. WT.
Barium	Ba	137
Bromine	Br	80
Calcium	Ca	40
Carbon	C	12
Chlorine	Cl	35.5
Copper (Cuprum)	Cu	63
Hydrogen	H	1
Iodine	I	127
Iron (Ferrum)	Fe	56
Lead (Plumbum)	Pb	207
Magnesium	Mg	24
Mercury (Hydrargyrum)	Hg	200
Nitrogen	N	14
Oxygen	O	16
Phosphorus	P	31
Potassium (Kalium)	K	39
Sodium (Natrium)	Na	23
Sulphur	S	32
Zinc	Zn	65

so, set free 44000 calories. The second one means that if 73 grams of hydrochloric acid were decomposed into 2 grams of hydrogen and 71 of chlorine, 44000 calories or their equivalent in some other form of energy would be absorbed and disappear as heat. In the first reaction the energy content of the matter ran down, and the action can be reversed only by restoring that energy to what it was at first.

The choice of the numbers 2, 71, 73, in the preceding paragraph, will be explained under the head of Gram-Molecule, page 68.

Radical groups whose compounds with one element are named with the suffix *ide*.
 HO Hydroxyl C.N. Cyanogen NH_4 Ammonium } *pr* groups.

CHAPTER XVIII

CHEMICAL NAMES

Suffixes and Prefixes play an important part in the system of naming that has been adopted for chemical compounds. The suffix *ide* in the name of a substance indicates that it is a compound and that it consists of two elements (a binary compound), thus HCl is hydrogen chloride, H_2O is oxide of hydrogen, CS_2 is sulphide of carbon. Compounds of the group HO with an element are known as *hydroxides*; thus NaHO is sodium hydroxide and $\text{Ca}(\text{HO})_2$ is calcium hydroxide. These are named as if they were binary compounds, because the substance HO (hydroxyl) acts as if it were a single element. It will be met with very often, as it plays a prominent part in a great many chemical reactions.

Prefixes are used in chemical names as follows: CO is called carbon *monoxide* to distinguish it from CO_2 , carbon *dioxide*; *mon* meaning one, and *di*, two; SO_2 is sulphur dioxide, but SO_3 is the *trioxide*. N_2O_3 is nitrogen *trioxide*, and N_2O_4 is nitrogen *tetroxide*, just as CCl_4 is carbon *tetrachloride*. P_2O_3 is phosphorus trioxide, and P_2O_5 is phosphorus *pentoxide* and PCl_5 is phosphorus *pentachloride*. The prefixes *mon*, *di* or *bi*, *tri*, *tetr* or *tetra*, *pent* or *penta* mean, respectively, one, two, three, four, five.

The names of acids end either in the syllable *ic* or *ous*. Formerly it was supposed that all acids contained oxygen, and those that have names ending in *ic* contain more oxygen in the molecule (but not any fixed number of atoms of it) than those formed from the same elements that have their names ending in *ous*. Thus H_2SO_4 is

sulphuric acid, and H_2SO_3 is sulphurous acid. HNO_3 is nitric acid, but HNO_2 is nitrous acid.

A salt, as already stated, is the compound resulting from the action of an acid with a metal, the oxide of a metal, or a base. Salts of the *ic* acid have names that end in the syllable *ate*, and salts of the *ous* acids have names ending in *ite*. H_2CO_3 is carbonic acid, and when the hydrogen is replaced by sodium from sodium hydroxide, thus $2\text{NaHO} + \text{H}_2\text{CO}_3 \rightarrow \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$, the salt is sodium carbonate. Similarly zinc with sulphuric acid produces ZnSO_4 , zinc sulphate. HNO_2 is nitrous acid, and H_2SO_3 is sulphurous acid; the salts of these with potassium have the formulæ respectively, KNO_2 and K_2SO_3 , and the names potassium nitrite and potassium sulphite.

Oxide of hydrogen is H_2O , but there is a second oxide having the composition H_2O_2 which is named hydrogen dioxide or hydrogen peroxide. The prefix *per* in such cases means *over*, or *above*, the normal; in the case of acids and salts it means *over* in regard to the quantity of oxygen in the molecule. Similarly *hypo* means *below*. For example, HClO_3 is chloric acid, but there is another acid whose formula is HClO_4 ; it is *perchloric* acid, and its salts are perchlorates. HNO_2 is the formula for nitrous acid, but the salt KNO is known, and it is evidently the potassium salt of an acid with a composition HNO ; the salt is then *hyponitrite* of potassium and the acid is *hyponitrous* acid.

The *acid radical* is that part of an acid molecule which remains after all the replaceable hydrogen has been displaced; this radical, then, must form part of the salt molecule also.

An acid and its salts resemble one another in having the radical common, but they differ in the former, having one or more atoms of hydrogen joined with the radical to make up the molecule, while the latter has one or more atoms of a metal. (Page 48.)

CHAPTER XIX

IONISATION

Dissociation is a term used to express the fact that, in some cases, compounds will separate into their constituents under special conditions, but, if the constituents are still in contact, they will reunite when these conditions are removed. For instance, water when heated above 1000° C. begins to separate into oxygen and hydrogen, and the dissociation goes on to a greater extent at higher temperatures. If the temperature be gradually reduced, the gases reunite, and at or below 1000° C. there is only water, as steam, present.

Experiment 57, in connection with many similar ones, illustrates these two general principles: (1) Metallic salts in water solution have very different properties in regard to electrical conductivity from those they possess when in the solid form. (2) Those substances classed as metals conduct electricity but do not themselves undergo any permanent change; some chemical compounds, however, when in the liquid state, either by solution or fusion, permit a current of electricity to pass through them, but they become decomposed in the process. These compounds are called **electrolytes**, and they consist of acids, bases and salts. Substances that do not belong to either of the above classes do not conduct electricity, hence are not electrolytes; sugar, glycerine, and the gums are examples.

When a salt in solution is subjected to the influence of the electric current, the metallic portion gathers at the

cathode and the acid radical at the anode. In the case of electrolysis of hydroxides, the hydroxyl radicals become concentrated at the anode, and when the electrolyte is an acid the hydrogen collects at the cathode. *Hydrogen and the metallic parts of the molecule move with the current, but the acid radicals and hydroxyl radical against it.*

This problem of the movement of matter in some solutions under the influence of the electric current was

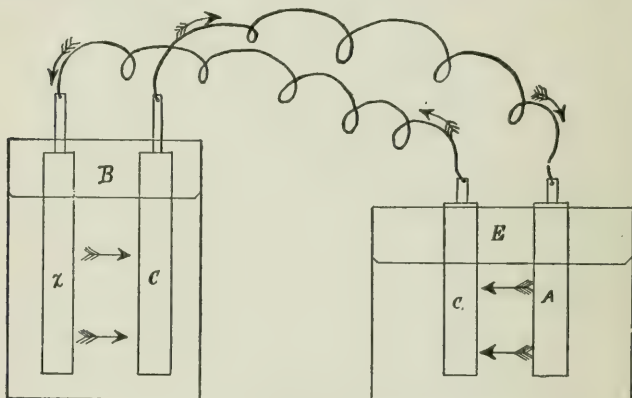


FIG. 4

Diagram showing direction of the current through an electrolytic cell.

B is the battery, Z the zinc plate, C the carbon or copper plate, E is the electrolytic cell, A is the anode, C the cathode.

long a puzzle to chemists, as were also the following: Two salts in solution will frequently react with each other, thus sodium carbonate and calcium chloride, both stable compounds, if mixed in solution, will produce calcium carbonate and sodium chloride; moreover such actions are gradual, not instantaneous. The question naturally arises as to when and why such reactions take place. To meet these and other unexplained difficulties of a similar nature the **Theory of Ionic Dis-**

sociation, or of **Electrolytic Dissociation in Solution** has been proposed.

Briefly this theory is the following:

(1) In an electrolyte some of the molecules become dissociated into parts. One of these parts consists either of the metallic or the hydrogen portion of the molecule, and the other of the acid radical, or the hydroxyl portion.

(2) A molecule thus dissociated does not form atoms, even though one of the parts may be of an elementary nature. The dissociated portions are named **ions**; and an ion is *matter plus electricity*. A metallic, or hydrogen, ion is always charged with positive electricity, and the other ion from a compound molecule carries an equal negative charge. In the nomenclature of this subject the prefix *an* means positive, and *cat* or *cath* negative; thus, anion and cation are the ions that move respectively to the positive and negative electrodes, that is, to the anode and cathode.

(3) Ions in solution may form combinations with others of the opposite electric kind. These unions produce molecules of matter that are electrically neutral.

(4) In the case of electrolysis of compounds the movement of the ions is accounted for by the well-known physical fact that bodies carrying charges of electricity of opposite kinds attract each other, while those charged in the same way repel each other.

(5) In an electrolyte the dissociation of the molecules goes on until a certain percentage of them, dependent on the particular substance, becomes ionised. When this stage is reached the process ceases, but if for any reason ions be removed, as when they enter into combination, the dissociation will continue. If, on the other hand, molecules be removed, as by precipitation or volatilisation, a further re-union of ions will occur.

The ions are represented by the symbols or formulæ that denote their material composition, with the arithmetical signs for positive or negative written over them to indicate the presence and kind of electric charge they carry. The plus and minus signs are often replaced by dots and dashes respectively, as in the following illustrations. The molecule of potassium nitrate ionises thus:

$\text{KNO}_3 = \overset{+}{\text{K}}, \overset{-}{\text{NO}_3}$ or $\overset{\cdot}{\text{K}}, \overset{\cdot}{\text{NO}_3}$, and that of sulphuric acid in this way $\overset{+}{\text{H}}, \overset{+}{\text{H}}, \overset{-}{\text{SO}_4}$ or $\overset{\cdot}{\text{H}}, \overset{\cdot}{\text{H}}, \overset{//}{\text{SO}_4}$.

When potassium nitrate dissolves in water, some of the molecules, but not all become dissociated—unless the solution is very dilute—so that there is in the water

$\overset{+}{\text{KNO}_3}$ and $\overset{-}{\text{K}}, \overset{-}{\text{NO}_3}$ bodies. If now a current is passed from the outside into the liquid by means of electrodes, the positively charged bodies will pass to the cathode. On reaching the oppositely charged plate, the ion gives up its electricity and becomes ordinary matter. The blue copper ions, for instance, that give solutions of copper salts their distinctive colour, change to red metallic copper that *is deposited on the cathode*.

If solutions of sodium hydroxide and sulphuric acid were mixed, the liquid would have in it $\text{NaHO}, \overset{\cdot}{\text{Na}}, \overset{\cdot}{\text{HO}}, \text{H}_2\text{SO}_4, \overset{\cdot}{\text{H}}, \overset{\cdot}{\text{H}}, \overset{//}{\text{SO}_4}$; and at once arises the possibility of unions among the ions to form *new molecules*; such combinations, however, can occur only between *ions oppositely charged and to an equal extent*. The new molecules would then be Na_2SO_4 and HHO or H_2O . This removes some of the ions from solution, and there will be further dissociation until the balance is re-established between all the ions and all the molecules present.

If, for any reason, molecules are continuously removed from the solution the dissociation that supplied the ions for those molecules will go on until the ionisation exhausts the substances; or, as it is generally expressed, the action will go on to completion. Such a case occurs when calcium chloride and sodium carbonate, two easily soluble salts, are dropped into a beaker of water. There are formed in solution from the original salts, CaCl_2 , Ca^{++} , Cl^- , Cl^- , Na_2CO_3 , Na^+ , Na^+ , CO_3^{--} . New combinations to produce CaCO_3 and NaCl will take place. The insoluble CaCO_3 is precipitated as fast as formed, so goes out of solution; that causes more Ca^{++} and CO_3^{--} ions to be formed, but these immediately combine and are precipitated; thus the action continues as long as substances are left that can furnish these ions.

All acids in solution separate into hydrogen and acid radical ions. For instance, H_2SO_4 into H^+ , H^+ , SO_4^{--} ; HNO_3 into H^+ , NO_3^- ; H_2CO_3 into H^+ , H^+ , CO_3^{--} and HCl into H^+ , Cl^- . *It is the essential characteristic of an acid that it shall, in solution, form hydrogen ions.* These constitute the replaceable hydrogen spoken of in a former paragraph. In a similar way bases ionise into metallic and hydroxyl ions; and the formation of the latter (HO^-) in solution *is the essential characteristic of a base.*

Recall now the Experiment, 58, in which copper sulphate was electrolysed. In that case copper ions were collected from all parts of the solution and deposited on the cathode, hence dissociation went on to completion. When the current was reversed, the copper atoms on the anode *gradually passed into solution as ions*, and made the journey to the cathode. This is typical of

the action of all metals. They assume the ionic condition preliminary to chemical union with substances in solution, such as acids.

Solutions of equal strength are those which contain equal numbers of molecules of the dissolved substances in equal volumes of the solution. The molecule of sodium hydroxide, NaHO is 40 times as heavy as an atom of hydrogen, and a molecule of sulphuric acid is 98 times as heavy as the same atom. It is clear then that 40 parts by weight of sodium hydroxide contain as many molecules as do 98 parts by weight of sulphuric acid; and if 40 parts by weight of the hydroxide were dissolved in water enough to make one litre, 1 c.c. of that solution would contain as many molecules of the solid as would 1 c.c. of sulphuric acid solution that had 98 parts by weight of acid per litre. A *molar solution* is one in which that number of grams of the solid expressed by its molecular weight (1 gram-molecule) is dissolved in water sufficient to make one litre of solution.

The terms *strong* and *weak* have various meanings, as applied to substances taking part in chemical actions. For instance, they are used to indicate chemical activity as measured by the rapidity with which substances act. In this sense nitric acid is strong and phosphoric acid weak. The expressions are often used, however, with reference to the stability of the compounds formed, especially in regard to changes of temperature. In this sense phosphoric acid is strong and nitric acid weak.

In this book the words will be used to denote rate of chemical action. That property is due to the extent that the molecules undergo dissociation in solution. A substance which has 70 per cent. of its molecules ionised will evidently act more rapidly than one that has only

10 per cent., in a solution of equal strength. As a matter of fact, nitric acid of a certain strength in solution dissociates to the extent of 90 per cent. of its molecules, hydrofluoric acid in an equally strong solution to 9 per cent., and carbonic acid in similar solution to twelve one-hundredths of one per cent. The relative numbers of hydrogen ions, then, in equal volumes of solutions of equal molar strength, will be 9000, 900, and 12. Therein lies the explanation of the great activity of the first as compared with the last substance; there are nearly 800 times as many ions ready to form new combinations.

The importance of the Theory of Electrolytic Dissociation in Solution, and the view generally held that chemical action between most inorganic substances when dissolved is ionic, not molecular, makes it necessary that learners should gain their knowledge of chemistry in terms of this theory, and that the simpler aspects of it should be presented very near the beginning of the study. Other points, especially those more difficult to deal with, may be deferred until occasion arises for their discussion. In the meantime this brief outline will serve to introduce the subject and afford the means for making applications of the different parts of it to simple problems.

PROBLEMS

1. Given that only hydroxyl ions are basic, and turn red litmus solution blue; and that only hydrogen ions are acidic, and turn blue litmus red, what interpretation is to be given to the observations on Experiments 56 and 59?

2. Heat a little potassium chlorate until oxygen ceases to come off. The reaction is expressed by the equation $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$. Dissolve, in separate vessels, in distilled water, a little of the original chlorate and of the substance, chloride, left in the tube, add a drop of silver nitrate solution to each.

What ions were present in each of the solutions after the silver nitrate was added? What new molecules would result from unions among these ions? Does KNO_3 give a precipitate in water? What molecules must have formed the precipitate? There was silver and chlorine in both mixtures. Why did the precipitate appear in one only?

Indicate by symbols the ions present if the following substances in solution were mixed. What new molecules could these ions form?

(1) H_2SO_4 and KHO , (2) HNO_3 and $\text{Ca}(\text{HO})_2$, (3) FeCl_2 and Na_2CO_3 , (4) NaHO and CaCl_2 , (5) KNO_3 and H_2SO_4 .

CHAPTER XX

EQUIVALENCE

Experiment 60 illustrates a method of determining the weights of different metals that are equivalent in combining power to one gram of hydrogen. Probably the results will be only approximately correct because of impure materials and lack of some precautions in the work, but the important thing to learn is that the same quantity of different elements combines with entirely different portions of a common substance. Thus the quantity of hydrogen set free from an acid by equal weights of different metals is not at all the same.

The experiment, when accurately done, with pure materials, and with precautions to avoid errors, leads to the conclusion that twelve grams of magnesium, or twenty-eight of iron, or thirty-two and a half of zinc, displace one gram of hydrogen from combination in acids. It has been found, too, Experiment 24, that .07 gram of sodium sets free 34 c.c.'s of hydrogen in water, or that one gram of the gas would be freed by 23 grams of the metal. Therefore, in combining or replacing power 23 grams of sodium is equal to 28 of iron, 12 of magnesium, 8 of oxygen, or 1 of hydrogen.

These numbers are called the **equivalents** or **chemical equivalents** of these elements.

The term equivalent may be defined as *that weight of an element which is equal in combining or displacing power to eight unit weights of oxygen, (or 1.01 parts of hydrogen).*

The eight parts by weight of oxygen are arrived at in the following way: Chemists have agreed to regard 16 parts by weight of oxygen as the standard for comparison for atomic weights, because when taking account of the different oxygen compounds they found that the single unit of oxygen entering into any of these compounds was approximately 16 times the weight of the former hydrogen unit. In such compounds as water, H_2O , and potassium oxide, K_2O , for each combining weight of hydrogen or potassium there is half a combining weight, or half of sixteen parts by weight, of oxygen, and this half combining weight has been selected as the standard of comparison for equivalence. It is that least quantity of oxygen by weight which in any of the oxides unites with a single combining weight of another element.

Equivalents and Atomic Weights.—In some cases equivalent weights and atomic weights are expressed by the same number. In other cases the latter is some simple multiple of the former. That is because in some compounds one combining weight (16 parts) of oxygen unite with two combining weights of the other element, as K_2O ; then one combining weight of that element (which is its atomic weight) is equal in combining power to one-half a combining weight of oxygen. In such compounds as MgO , the atomic weight of magnesium is twice the equivalent, because one combining weight of magnesium unites with twice eight parts by weight of oxygen. In the compound Al_2O_3 the atomic weight of aluminium is three times the equivalent. In determining the atomic weight of an element, chemists examine all available compounds of the substance under consideration, and they select the smallest mass that enters into any combination as the unit combining weight or atomic weight.

CHAPTER XXI

VALENCY

If calcium chloride and sodium sulphate be mixed in solution there will be present the following molecules and ions in the liquid: CaCl_2 , Na_2SO_4 , $\overset{\cdot}{\underset{\cdot}{\text{Ca}}}$, $\overset{/}{\text{Cl}}$, $\overset{\cdot}{\text{Na}}$, $\overset{//}{\text{SO}_4}$. One meeting this notation for the first time will doubtless be puzzled to know why some ions are represented as carrying double charges of electricity, and others but single ones. Unfortunately, the question must remain unanswered, for, at the present time, it is one of the unsolved problems of chemistry. Inability to account for the phenomenon does not interfere with the known fact that the calcium ion will enter into union with *one* SO_4 ion, which bears two unit charges of the electricity of the opposite kind to its own, or will combine with *two* ions of the Cl type, but not with *one* of the latter. Thus the new molecules may be CaSO_4 , but not CaCl ; and may be NaCl , but not Na_2Cl nor NaCl_2 . Ions enter into combination, then, with others of opposite electrification, and the proportions by number in which they combine are such that the electrical charges neutralise each other. This quantitative relation has reference only to the numbers of ions that unite to form a molecule, and not at all to the intensity of the attraction that holds them together; thus H_2CO_3 , NaHCO_3 and Na_2CO_3 are compounds of similar structure, of which the first one is readily decomposed at ordinary temperatures, the second at the temperature of a baker's oven, while the third is stable at a red heat.

When elements unite under conditions in which there is no solution in the ordinary sense, as hydrogen burning with oxygen, the same numerical relation holds among the combining atoms that did in the case of the ions of these elements. Thus one atom of oxygen will hold in combination two atoms of sodium, and only two; it will also unite with one atom of calcium, and only one; and in such cases the combining power of the atom is said to be satisfied.

Valency, or valence, is the term used to express the combining power of an atom of an element for atoms of other elements, the power of an atom of hydrogen being the unit. Combining power is here used for the attractive force that causes atoms to unite, and holds them in groups or molecules. This attractive force is measured by the number of atoms held, not by the intensity with which it acts.

An element is monovalent, or a monad, if one atom of it forms a stable compound with one atom of hydrogen or of another monad, or if it displaces one atom of either of these from combination. HCl , KCl , and KI are formulæ of compounds in which chlorine, potassium and iodine are monads. An element is divalent, or a diad, if an atom of it will unite with two atoms of hydrogen or of another monad, or will displace them from compounds. H_2O , CuO , H_2S , are formulæ of compounds in which oxygen, copper and sulphur are diads. Elements are thus classed as monovalent or monads, divalent or diads, trivalent or triads, etc.

Substances of equal valency combine in equal proportions, but when the valencies are unequal, the number of atoms entering into the union are such that the valencies balance. Thus aluminium is a triad and oxygen is a diad, then two atoms of the former have the same number

of combining powers as three of the latter and aluminium oxide is Al_2O_3 .

The valency of some elements varies at times with the conditions under which chemical action takes place. For instance, sulphur forms the compounds H_2S , SO_2 , SO_3 , in which its valency is respectively 2, 4 and 6. In combination with hydrogen and most metals, sulphur is a diad, burning in oxygen it acts as a tetrad, and in sulphates it is hexavalent. In the following list a few of the common elements are grouped according to their valencies; and in case a substance occurs more than once the conditions under which it has one or other combining power must be learned by experience. A substance, however, has its highest valency in its *ic* compounds, as nitrogen in nitric acid and the nitrates, sulphur in sulphuric acid and the sulphates, and iron in ferric compounds.

Monads—potassium, sodium, silver, chlorine, bromine, iodine.

Diads—calcium, barium, magnesium, zinc, iron, copper, lead, tin, oxygen, sulphur.

Triads—nitrogen, phosphorus, arsenic, aluminium, boron, iron.

Tetrads—carbon, sulphur, silicon, lead, tin.

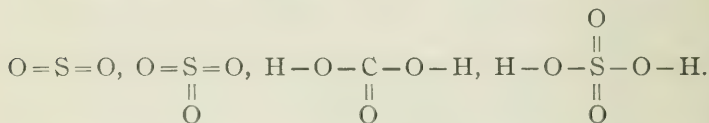
Pentads—nitrogen, phosphorus, arsenic.

Hexads—sulphur.

CHAPTER XXII

GRAPHIC FORMULÆ

One system of notation represents the number of combining powers, or bonds of attachment of the atoms by dashes, and it is convenient at times to express valency in this way. It must not be assumed, however, that these lines represent either the arrangement of atoms within the molecule, or the strength of the attractive force that holds them together. The following groups are the formulæ for sodium chloride, water, sulphur dioxide, sulphur trioxide, carbonic acid and sulphuric acid. Na-Cl, monad atoms held by a single bond. H-O-H, the atom of oxygen, with two bonds, those of hydrogen with one.



Such formulæ represent molecular structure in only one particular, the number of atoms and their valencies.

CHAPTER XXIII

WRITING EQUATIONS

Generally an equation in chemistry represents two things: the reaction, so far as known, that occurs between the substances, and the final products of that reaction. Such an expression as $\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaHO} + \text{H}$ indicates clearly enough the replacement of hydrogen by sodium; but no such quantity of matter as that represented by H has an independent existence. Such a quantity does take part in chemical action, and it is displaced from compounds, but it does not remain a free mass. The smallest part of hydrogen that has a permanent and separate existence is represented by H_2 , the molecule of two atoms. If, then, the foregoing equation is to represent the substances resulting from the reaction it must be written $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaHO} + \text{H}_2$. Such an expression is a *molecular equation*, to distinguish it from that form of equation that represents the reaction only. Oxygen, hydrogen, nitrogen and chlorine, the elements that are gaseous at ordinary temperatures, all exist in the form of molecules consisting of two atoms. (See Vapour Density.) O_2 , not O, represents oxygen gas; Cl_2 , not Cl, is chlorine, and N_2 is nitrogen.

If oxygen is prepared from potassium chlorate, the equation $\text{KClO}_3 \rightarrow \text{KCl} + 3\text{O}$ represents the molecular disintegration, but it does not represent the molecular rearrangement, for 3O stands for three separate atoms of oxygen, but that gas exists free only as molecules of two atoms each. The quantities will therefore have to

be doubled, thus, $2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$. All equations in which it is necessary to represent any elementary gaseous substance as having free existence must be written in the molecular form.

PROBLEMS

1. Write the symbols for the ions and the formulæ for the new molecules that would be formed if solutions of the following pairs of substances were mixed, given that HNO_3 , H_2CO_3 , HCl and H_2SO_4 are respectively nitric, carbonic, hydrochloric and sulphuric acids.

(1) KHO and HNO_3 ; (2) NaHO and HCl ; (3) $\text{Ca}(\text{HO})_2$ and H_2CO_3 ; (4) KHO and H_2SO_4 ; (5) CaCl_2 and H_2SO_4 ; (6) $\text{Mg}(\text{HO})_2$ and HCl ; (7) Na_2CO_3 and $\text{Ca}(\text{HO})_2$; (8) Na_2CO_3 and H_2SO_4 ; (9) KHO and H_2CO_3 ; (10) AgNO_3 and KCl ; (11) AgNO_3 and KClO_3 ; (12) CuSO_4 and $\text{Ca}(\text{HO})_2$.

2. Write the names of the compounds represented by the formulæ in the previous problem, also the names of all the new compounds formed.

3. Write the formulæ for the oxide, hydroxide, carbonate, sulphate, chloride, nitrate, and sulphide of each of the following metals: Potassium, sodium, calcium, barium, magnesium, zinc, copper, and lead (diad).

4. Write equations for the following reactions:

(1) Hydrogen is obtained from water by electrolysis.

(2) Hydrogen is prepared from zinc and sulphuric acid.

(3) Hydrogen is obtained from magnesium and hydrochloric acid.

(4) Oxide of mercury is decomposed by heat.

(5) Magnesium burns in air.

(6) Carbon burns in oxygen to carbon dioxide.

(7) Hydrogen burns in oxygen to water.

(8) Air is passed over red-hot copper.

- (9) Hydrogen is passed over red-hot copper oxide.
- (10) Magnesium burns in steam.
- (11) The action of steam on hot iron to form Fe_3O_4 .
- (12) The neutralisation of hydrochloric acid with sodium hydroxide (caustic soda).
- (13) The neutralisation of sulphuric acid with sodium hydroxide.
- (14) Sulphur burns in oxygen (sulphur is a tetrad).
- (15) Phosphorus burns in oxygen (phosphorus is a pentad).

CHAPTER XXIV

NITROGEN

It has been shown that air consists of a mixture of two gases; one of these is oxygen. In Experiments 35, 41, 42 and 61, the gas that remained in the jar was **Nitrogen**, an element that enters into few combinations, and is rather inactive. It exists free in the air, of which it forms approximately 79% by volume. It is an essential constituent of most living matter, and it occurs also in some minerals.

Preparation.—Nitrogen is generally obtained by removing oxygen from the air. It is necessary, however, that if an oxide is formed in the process it should be easily separable from the nitrogen either by precipitation or by solution. When phosphorus is used for this purpose the nitrogen is never pure, as combustion ceases before all the oxygen is taken up, and the foreign ingredients of the atmosphere are not removed. When the gas is wanted quite pure it is obtained by decomposing ammonium nitrite, thus, $\text{NH}_4\text{NO}_2 \rightarrow 2\text{H}_2\text{O} + \text{N}_2$. Air drawn slowly over heated copper, then passed through an alkaline solution of pyrogallic acid furnishes nitrogen nearly pure.

Properties.—Nitrogen does not burn, does not support combustion, is scarcely at all soluble, does not affect litmus, and unites directly with but few other elements. It combines slightly with oxygen under the influence of powerful electric discharges, and it unites with hot magnesium to produce a nitride of that metal.

Uses.—In the laboratory, nitrogen is used as a gas in which to immerse substances that are to be heated without undergoing oxidation. It is necessary for plant growth, but for this purpose the free nitrogen of the atmosphere is useless. To be serviceable it must be *fixed*; that is, formed into some compound that may be dissolved in water and absorbed by the roots of the plants. At the present time certain groups of bacteria, notably those that cluster on the leguminous plants, seem to be the most effective agencies for the fixation of nitrogen. Efforts are being made to devise some plan of cheaply fixing the nitrogen of the atmosphere by artificial means. Most fertilisers owe their nitrogen to matters of organic origin—as guano, barnyard manures, and nitrates formed in waters and soil, through decaying animal and vegetable substances.

CHAPTER XXV

NITRIC ACID

Generally a less volatile acid may be made to displace a more volatile one from its combinations. On this account sulphuric acid may be used as an agent to set free other common acids from their salts, among these nitric acid, as in Experiment 62.

Potassium nitrate with sulphuric acid produces nitric acid, thus, $\text{KNO}_3 + \text{H}_2\text{SO}_4 = \text{KHSO}_4 + \text{HNO}_3$. If the mixture be heated the nitric acid passes off as vapour, and may be condensed to a liquid at the temperature of cold water. Nitric acid, the *aqua fortis* of the alchemists, is an exceedingly active *monobasic* acid. It is active because in solution a very large percentage of its molecules undergo ionisation; and it is monobasic because in the process of dissociation in solution, one, and only one, hydrogen ion splits off from each molecule. (Compare Chapter XLV.)

Nitric acid is an energetic oxidising agent, as it readily undergoes decomposition, thus, $4\text{HNO}_3 \rightarrow 2\text{H}_2\text{O} + 4\text{NO}_2 + \text{O}_2$, or $4\text{HNO}_3 = 2\text{H}_2\text{O} + 4\text{NO} + 3\text{O}_2$.

On account of its instability, and its tendency to oxidise substances with which it is in contact, nitric acid does not yield free hydrogen when acted on by metals, except in the case of magnesium. Experiment 67 is an illustration of this, and at least two important phases of the reaction are symbolised by the equations $\text{Zn} + 2\text{HNO}_3 \rightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{H}$, and $2\text{H} + 2\text{HNO}_3 \rightarrow 2\text{H}_2\text{O} + 2\text{NO}_2$. Hydrogen is certainly displaced from the acid by the metal, but just as certainly it is an oxide of nitrogen

that comes off. There must, then, have been a second reaction, in which the hydrogen entered into some combination to set the other gas free. The second equation represents one of the possible reactions that may occur, in which the hydrogen is oxidised to water, and some of the excess of the acid is reduced to nitrogen peroxide. Such conditions, however, as temperature, and concentration of reacting materials, modify the rate at which hydrogen is set free, and the reduction of the acid may be carried to various degrees, as $4\text{H} + 2\text{HNO}_3 = 3\text{H}_2\text{O} + \text{N}_2\text{O}_3$, and $6\text{H} + 2\text{HNO}_3 = 4\text{H}_2\text{O} + 2\text{NO}$. In practice it is found that generally several of those reactions go on together, and a mixture of oxides of nitrogen is formed.

It should be noted that this oxidation of hydrogen occurs only when the element is *set free from combination in presence of the acid*. Hydrogen that has been prepared in the ordinary way has no appreciable effect on the acid when passed into it. An element that acts as hydrogen does here is said to be *nascent*, or in the *nascent condition*. This is a technical term, formerly used to describe a hypothetical condition in which the substance was supposed to have been set free as individual atoms, and these formed combinations either with each other or with some other matter present, preferably with the latter. What really does go on is a matter of conjecture only; and since there are serious difficulties in the way of accepting the former theory, it seems safer just to state the fact that the setting free of one element in presence of other substances may disturb the chemical equilibrium in such a way as to set up a second reaction.

Other examples of energetic chemical action due to the nascent condition of elements will be found under Chlorine, Hydrogen Dioxide, and Sulphur Dioxide.

Nitrates are all soluble in water, hence they are found as minerals only in situations in which they are protected from this solvent action. For example, there is a rainless valley in Northern Chili that contains the largest known deposits of nitrates, and from which immense quantities are shipped to Europe to be made into land fertilisers, or to be used in the manufacture of nitric acid.

The nitrates are unstable compounds, and like nitric acid they are decomposed when heated, setting oxygen free. The nitrates of the alkaline metals become reduced to the nitrites when heated, and those of the heavy metals to the oxide of the metal. Thus, if lead nitrate or copper nitrate be heated in a hard glass test tube the oxide will remain.

The nitrates, particularly of potassium and sodium, are used as sources of oxygen, especially in cases in which it is desirable that the oxidation should proceed rapidly throughout the mass, as in gunpowder.

A somewhat rough test for the presence of nitric acid is made by mixing some of the liquid with enough solution of indigo to make the whole distinctly blue, then heating the mixture. If the blue colour disappears nitric acid is present. The brown fumes given off by a liquid when boiled with copper, also indicate the presence of this acid. Either a nitrate or nitric acid may be tested for as follows: Put some water mixed with a little sulphuric acid in a clean evaporating dish, cool it well and drop into it a crystal of iron sulphate (copperas). Bring the point of a pipette that contains some of the liquid to be tested close to the sulphate crystal, and let the liquid escape slowly. If, in a few minutes, a greenish brown sediment appears, the liquid contained nitric acid, or a nitrate that set nitric acid free in the presence of the sulphuric acid.

CHAPTER XXVI

OXIDES OF NITROGEN

The deep brown gas formed either when nitric acid is heated above the decomposition temperature, or when the strong acid acts with metals, is nitrogen peroxide or tetroxide, NO_2 or N_2O_4 . When it has the former composition (above 140°C.), it should be named peroxide, and when the latter, should be called tetroxide; but in usage the terms are interchangeable. Experiments 62-66 illustrate the formation of the tetroxide either as NO_2 or N_2O_4 , while in Experiment 67 it came off mingled with nitric oxide, NO . The brown gas being readily soluble may be easily separated from the other, and the admission of oxygen to the latter causes it to be oxidised to N_2O_4 , as shown by the change of colour and solubility.

The colourless gas that was collected over water, Experiment 69, was nitric oxide, NO , or nitrogen dioxide. It is one of the substances that generally is formed by the action of nascent hydrogen or nitric acid; it also is produced when nitrogen peroxide is deprived of half its oxygen. The importance of nitric oxide depends on its capacity for combining with oxygen by mere contact to form the peroxide (see the preparation of sulphuric acid).

When nitrates of the alkalies are heated they are easily reduced to the corresponding nitrites and free oxygen, thus $2\text{KNO}_3 = 2\text{KNO}_2 + \text{O}_2$; but in the case of ammonium nitrate the decomposition goes farther and the hydrogen is oxidised to water, thus, $\text{NH}_4\text{NO}_3 = 2\text{H}_2\text{O} + \text{N}_2\text{O}$. The most important property of the gas N_2O , nitrous oxide, is

its ability to support combustion almost as freely as oxygen itself. In order to do this the compound must be decomposed, because only free oxygen enters into combination with such substances as carbon and phosphorus when they burn. This leads to the conclusion that N_2O is an unstable compound that may be decomposed by the heat of a burning splinter; and, in consequence, it acts readily as an oxidiser. It is distinguished from oxygen by its solubility. Nitrous oxide was formerly much used as an anæsthetic, especially by dentists. A popular name for it is *Laughing Gas*, because of the effect it produces when inhaled in quantity.

We have now had three oxides of nitrogen prepared, and there are two others that are not of sufficient importance to consider at the present time. The full series is:

N_2O *Nitrous Oxide*, or Nitrogen Monoxide.

NO *Nitric Oxide*, or Nitrogen Dioxide.

N_2O_3 *Nitrogen Trioxide*, or Nitrous Anhydride.

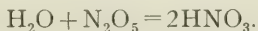
NO_2 *Nitrogen Peroxide*, or Nitrogen Tetroxide.

N_2O_5 *Nitrogen Pentoxide*, or Nitric Anhydride.

When alternative names are allowed, those given in italics are the preferable ones to use to avoid confusion. The terms dioxide and tetroxide for the second and fourth numbers of the series have persisted from a time when the compounds were thought to be represented by the formulæ N_2O_2 and N_2O_4 . As a matter of fact, the peroxide at low temperatures has an atomic grouping represented by N_2O_4 ; but, as the gas becomes heated, these molecules divide, each into two parts, and at about 140° C. the dissociation is complete, so that above that temperature the formula for the gas is NO_2 . The substance called peroxide or tetroxide of nitrogen is generally a mixture of NO_2 and N_2O_4 , in which one or other

predominates according to the temperature. (See Vapour Density.)

Anhydrides.—The pentoxide and trioxide of nitrogen when dissolved separately in water form respectively nitric and nitrous acids, thus,—



An oxide that forms an acid solution with water is classed as an *anhydride*, so that the oxides of nitrogen just mentioned are spoken of as nitric and nitrous anhydrides. Other examples of anhydrides are sulphur dioxide, sulphur trioxide, carbon dioxide, and phosphorus pentoxide.

PROBLEMS

1. Boil a little red lead with strong nitric acid.

What change comes over the appearance of the solid? Dry the brown powder and try whether it or the red lead gives off oxygen more freely. Red lead is Pb_3O_4 , brown lead oxide is PbO_2 ; which is the higher oxide? What chemical change occurred? Write the equation.

2. Heat a little concentrated nitric acid to boiling in a flask, drop in a piece of copper and close the flask with a glass plate. When the glass is filled with dense brown fumes, lower into it a piece of burning phosphorus on a chalk cup.

Does the rate of combustion of the phosphorus change? Assuming that P_2O_5 is formed, write the equation for the reaction. Describe the chemical reactions as cases of oxidation and reduction.

When the phosphorus ceases burning, invert the flask over water; and, after the gas clears, slip a glass plate under the mouth of the flask and turn it over without allowing air to enter it.

Will the gas now in the flask support combustion? What happens when air is admitted? Where did the transparent gas come from? How could it be determined whether the action of the phosphorus produced nitric oxide?

CHAPTER XXVII

AMMONIA

Sources.—It has long been known that if animal substances, rich in nitrogen, such as flesh, horn and skin, be heated out of contact with the air, there will be given off, among other substances, a pungent smelling, soluble gas that is strongly basic. This is called ammonia, and the druggist's names for it when dissolved in water are *Liquor Ammoniaë*, *Aqua Ammonia*, or *Spirits of Hartshorn*.

At the present time the world's supply of ammonia is obtained as a by-product in the preparation of illuminating gas. The coal used for this purpose generally contains from 1.5 to 2.25 per cent. of nitrogen, and in the process of distillation some of this combines with hydrogen, also found in the coal, to form ammonia, NH_3 . The gaseous products of the coal are washed in cold water, as they come from the retort, and the ammonia with some other substances are held in solution. The wash water is then boiled with lime, and the expelled gas is led into a solution of hydrochloric or sulphuric acid. (Refer to Experiment 118, Manual.) The salt formed in solution is recovered by evaporation.

Preparation.—In order to prepare ammonia, advantage is taken of the fact that it is displaced from its combinations by alkaline bases. For instance, $\text{NaHO} + \text{NH}_4\text{Cl} = \text{NaCl} + \text{NH}_4\text{HO}$, and $\text{NH}_4\text{HO} \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$.

If then an ammonium salt be treated with an alkaline hydroxide (or oxide in presence of water), ammonia gas will be formed, and as soon as the water present becomes saturated with the gas the excess of the latter will pass off.

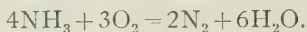
Properties of Ammonia.—Ammonia is soluble to a marked extent in water, as shown in Experiment 73. At 0° C. and at a pressure of one atmosphere water will dissolve more than 1,100 times its own volume of ammonia gas. The liquid sold in the drug stores as ammonia or hartshorn is a strong solution of the gas in water. This serves as a convenient source for a laboratory supply of ammonia, which is given off freely on heating the liquid.

When ammonia is brought into contact with water the two enter into combination to some extent to form NH_4HO , ammonium hydroxide. Commonly this is called a solution of ammonia, but it is more than this, because it has basic properties, therefore it must contain HO ions. It forms salts with acids, and in these salts the hydrogen of the acid is replaced by NH_4 ; hence, the so-called solution contains two kinds of ions, NH_4 and HO , and these could only have been formed by the dissociation of molecules having the composition NH_4HO , which resulted from the union of ammonia and water. A large portion of the gas that passes into the water remains simply in solution, so that there is only a small quantity of base, at any one time, as compared with the unchanged ammonia in solution. The action between the gas and the water, however, is a reversible one, and the direction in which it goes is dependent mainly on temperature, pressure, and concentration. If NH_4HO is removed more ammonia will combine with water to supply the loss, and the action may go on to completion; while if ammonia be driven out of solution by heat or reduced pressure, the hydroxide will gradually decompose into the original gas and water.

It is important in this connection to keep in mind that the hydrogen of acids is replaced not by *ammonia*, NH_3 , but by *ammonium*, NH_4 . The salts formed are

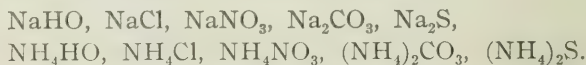
therefore not compounds of the former substance, but of the latter. Confusion regarding this matter arises from ammonia gas being set free from these salts, and from solution of ammonia neutralising acids. The ammonia gas is the result, however, of a secondary reaction—the decomposition of ammonium hydroxide produced in the first case from the ammonium salt—and the neutralisation is due to the compound formed by ammonia and water, NH_4HO , an alkaline base.

Commonly, ammonia will not burn, but if it be heated in contact with hot air it will undergo a fitful combustion, Experiment 71, and when mixed with oxygen and ignited, it burns to water and nitrogen, Experiment 72. This may be shown either by mixing the dry gases in a vessel and holding a flame to the mouth of it; or by passing oxygen through the inner tube of an oxyhydrogen burner and ammonia through the outer one, then igniting the gases at the jet.



Ammonia is lighter than air, having a density of .59, when air is taken as the standard; on this account it is usually collected by displacement of air downwards.

The radical NH_4 , which acts as a metal in chemical combinations, is known by the name **Ammonium**. It forms compounds similar to those of the alkaline metals, as will be seen from the following examples:



It is clear from the illustrations, especially from the compound NH_4HO , that ammonium acts as a monovalent radical. This fact is sometimes expressed in another way, thus,—in the radical NH_4 nitrogen acts as

a pentad, four of whose bonds are satisfied by the hydrogen atoms, and one is still free to attach the group in any suitable combination.

Neither ammonium nor its hydroxide can be separated from solution without undergoing decomposition into ammonia and water. While the following experiment is not entirely convincing, it affords ground for considering that ammonium has the properties of a metal. Many metals form solutions, known as amalgams, with mercury, and only metals are dissolved in this way:

EXPERIMENT III. Make some sodium amalgam by dropping small pieces of sodium into hot mercury, then place this amalgam, after it cools, in a strong solution of ammonium chloride.

What change comes over the amalgam? What gas escapes from the liquid? What taste does the liquid acquire? What does the spongy, metallic mass feel like? Lift the swollen mass of metal out of the liquid, and find if ammonia escapes from it?

It is believed that in this reaction the ammonium from the NH_4Cl and the sodium of the amalgam replace each other, forming NaCl and ammonium amalgam; the latter, being unstable, breaks down into ammonia, hydrogen and mercury. The swelling of the mass is due to the formation of bubbles of gas in its interior.

The conclusion from the above Experiment is somewhat strengthened by electrolysing a solution of an ammonium salt, and making the cathode consist of a drop of mercury into which the proper battery wire dips.

The debatable point in both cases is whether the spongy, soapy mass is a real amalgam, and the instability of the substance makes this a difficult question to settle.

Uses of Ammonia.—Ammonia gas at 0°C . liquefies

under a pressure of about four and a half atmospheres, and in so doing sets free a large quantity of heat, about 260 calories per gram; and, of course, when the operation is reversed this amount of heat must be supplied. Advantage is taken of this in making artificial ice and in refrigerating appliances. Ammonia in a series of closed pipes is first condensed to the liquid state, and the heat set free is carried off by running water. The liquid ammonia is conveyed to a part of the apparatus where the

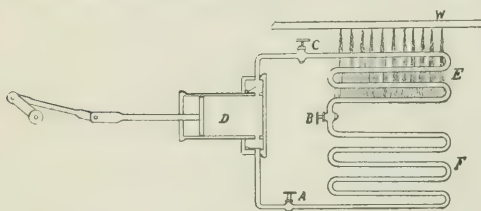


FIG. 5

Diagram of an ammonia cooling plant.

Suppose the valve B is closed, the pipes F filled with liquid ammonia, and the pump withdrawing this as it vapourises under reduced pressure and driving it into E. W is a water pipe from which streams of water drip over E to carry off the heat of condensation. When E is filled with liquid ammonia the valves C and A are closed, B is opened and the liquid flows into F, to be again withdrawn.

cooling or freezing is to be done, and the pressure is reduced by pumping the vapour back into the condenser; the heat required for this vapourisation is absorbed from the surrounding materials. In ice making, for in-

stance, the pipes are immersed in a vat of brine, in which are placed cans containing the water to be frozen. Heat is absorbed from the brine until its temperature is below the freezing point of pure water.

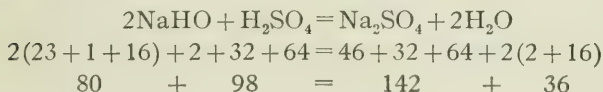
Ammonia is used in household operations as a solvent for grease, with which it forms soluble compounds; and in the laboratory, where it is employed to neutralise acids. While it is distinctly a base when in solution, it is a weak one, and thus is preferable in many cases to those of the strongly alkaline metals such as sodium and potassium.

CHAPTER XXVIII

QUANTITATIVE RESULTS IN CHEMICAL REACTIONS

Since substances take part in chemical actions only in definite proportions by weight it becomes an easy matter to work out the quantitative results when the character of the reaction is known. For instance, $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ means that four unit weights of hydrogen, combine with thirty-two of oxygen to form thirty-six unit weights of water; or, expressed in their simplest proportions, these numbers become, respectively, one, eight, and nine. It follows then that nine unit weights of water, when decomposed, will yield one unit of hydrogen and eight of oxygen.

In the experiment in which sodium hydroxide solution was neutralised by sulphuric acid, the quantitative calculation would be as follows:



Eighty unit weights of the hydroxide combine with ninety-eight of the acid to produce one hundred and forty-two of the sodium sulphate and thirty-six of water.

When a reaction between two substances ceases because one is entirely used up but the other not, that one of which a portion still remains is said to have been present in *excess*, and the extent of the reaction is limited by the quantity of the one which enters entirely into combination.

PROBLEMS

1. Calculate the percentage composition of the following substances, that is, what per cent. by weight each element is of the compound into which it enters: H_2O , NH_3 , NH_4HO , NH_4NO_3 , HgO , KClO_3 , SO_2 , CO_2 .

2. How much hydrogen, by weight, will be set free by 65 grams of zinc acting (1) on excess of sulphuric acid; (2) on excess of hydrochloric acid?

3. If (1) 6.5 grams and (2) .65 grams of zinc had been used in the previous question what would the answers have been?

4. What weight of nitric acid can be obtained from 9.8 grams of sulphuric acid acting on excess of potassium nitrate?

5. What weight of nitric acid will be set free by excess of sulphuric acid acting on 10.1 grams of potassium nitrate?

6. If 4.4 grams of nitrous oxide were required, how many grams of ammonium nitrate should be taken to prepare it?

7. An evaporating dish weighs 22.3 grams; some water was put into it, and sodium added in small pieces. The water was then evaporated and the dish with the dry solid weighed 24.3 grams. What weight of sodium was added to the water?

8. What weight of water would combine with 2.3 grams sodium to form sodium hydroxide, and what would the latter compound weigh?

9. When copper dust is heated in a tube in a current of air, by what fraction can its weight be increased? What percentage increase is this of the original copper?

10. If phosphorus were burned in nitrous oxide and the fumes dissolved, what gas would remain?

11. Nitrous oxide is mixed in a eudiometer with the proper quantity of hydrogen to complete the chemical action, and the mixture ignited; what will remain?

12. A tube is filled with nitric oxide and inverted in water; oxygen is then very gradually admitted. Describe what will take place in the tube. Confirm the answer by making the experiment.

13. A tube has some nitric oxide in it and is standing inverted in water; air is gradually passed in. What will happen in the tube? Will any gas remain when the chemical action ceases? If so, what will it be?

14. When a piece of copper is dropped into concentrated nitric acid why does the chemical action increase in intensity as it progresses?

15. In a certain operation it became necessary to heat a substance in a current of nitrogen. To secure the gas for this purpose a piece of iron tubing was loosely packed with copper turnings, placed in a furnace and one end connected with the tube containing the material to be heated. Air was forced through the whole after the tube containing the copper became red hot. Explain the chemical action involved.

CHAPTER XXIX

RATE OF CHEMICAL REACTION

Experience shows that the quantity of chemical action that occurs in a given time may be very variable even when the reacting substances are the same. Experiments 74-77 illustrate this. In 74 (b) the acids were of like strength, the marble of the same composition, yet an alteration of temperature changed the rate at which the reaction went on. In 74 (c) the physical state of the marble affected the result. This might reasonably be expected for the reason that chemical action occurs only at the contact surfaces of the reacting substances. The powder exposed a far larger surface to the surrounding liquid than the lump did; and in 75, the dissolving of one of the solid masses was a device for getting it into the finest possible state of division, and thus exposing it to instantaneous action with the acid, as far as that could be done. If all parts of the two liquids could be brought into contact at the same moment the reaction would be of the nature of an explosion, because of the large volume of gas suddenly liberated. Experiment 68 is another example of this same means, viz.: Increase of surface contact, to hasten the rate of reaction. Experiment 74 (a) shows that the degree of concentration, that is, the quantity of reacting substance per unit volume, may affect the rate of change. Indeed this alteration may result from two causes; not only will there be a different number of ions per unit mass capable of reacting, but the energy set free, or absorbed as heat, may modify the rate

at which the change goes on. A case of this kind occurs when copper is dropped into concentrated nitric acid.

In Experiment 77 all conditions, save the action of light, are the same for the two solutions. Difference in the result, therefore, shows that one action has proceeded a measurable distance when tested, and that the other has not. It does not prove that there was no chemical change in the liquid from which light was excluded; it shows, however, that it had not gone far enough to be detected by the starch test.

It has thus been shown that the rate of chemical reaction can be varied in many cases by proper treatment, and that within certain limits the speed can be controlled. The means commonly employed for this purpose are change of concentration, change of temperature, use of light and of the electric current, and alteration in the condition of aggregation.

Change of concentration is generally effected by dilution, or by removal of the diluting material. Acids, for instance, may be mixed with water; oxygen with nitrogen or carbon dioxide; and sodium with mercury. Change in the state of aggregation may vary all the way from a single mass of the substance to the separated molecules as they exist in solution.

It may be noted in this connection that to intimately mix reacting substances is to have recourse practically to the method of solution, for it is a device to bring them into contact at many points throughout the mass. If it were possible, for instance, to grind charcoal to exceeding fineness, and then surround every particle with oxygen and heat it to the kindling temperature, combustion would be extremely rapid. An approach to this hypothetical condition is made in the case of gun cotton and gunpowder, in which the combustible materials are brought

into the closest possible connection at every part with a substance capable of supplying the necessary oxygen.

In modern Chemistry the varying activity due to concentration is sometimes spoken of as *mass action*: the term mass not being used in relation to the whole quantity of reacting matter present, but to the quantity per unit volume. Thus whether hydrogen takes oxygen away from iron with which it is combined, or iron takes oxygen away from hydrogen with which it is united, turns on whether hydrogen is concentrated in presence of iron oxide or iron in presence of hydrogen oxide.

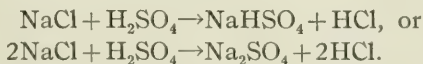
CHAPTER XXX

HYDROGEN CHLORIDE

Hydrogen and chlorine may be made to unite and form hydrogen chloride (Experiment 83). It is also produced when hydrogen ions and chlorine ions exist in the same solution. The preparation of the compound in quantities suitable for laboratory purposes depends on the ionisation of proper materials. Some binary compound of chlorine, as the chloride of sodium or of calcium, is generally chosen as a convenient substance to use, and since hydrogen chloride is gaseous at ordinary temperatures and generally passes off as soon as formed, the less volatile sulphuric acid will furnish the hydrogen ions,



From this either of the following reactions may occur:



If the sulphuric acid is largely in excess the first reaction occurs; but if there is sufficient of the sodium chloride the second reaction takes place. (See Basicity of Acids, Chapter XLV.)

Hydrogen chloride is a pungent, acid-smelling gas, heavier than air, very soluble, and neither burns nor supports combustion. In moist air it causes the vapour of water to condense into mist drops, thus producing a white cloud. The gas is very stable, but is easily liquefied.

Experiment 81 shows that hydrogen chloride possesses certain properties in water solution which it has not when dissolved in oil, because in the latter case it is not an electrolyte and it does not act with marble. It is a property of all acids that, in their solutions, ions of hydrogen and of the acid radical exist and that these may be concentrated at the electrodes by which a current passes into and out of the liquid. The oil solution of hydrogen chloride is not an electrolyte, because it does not contain free ions, hence is not an acid; moreover, it does not exhibit other acid properties such as that shown in the action of the water solution with marble.

Investigations prove that neither the dried gas, nor the liquid which it forms when condensed, nor the solution of the gas in benzine, coal oil, chloroform or gasoline, shows any acid properties; but that the solution in water is actively acid. The moisture of the air and that condensed on the surface of many substances will dissolve enough of the gas to show an acid reaction, litmus paper is an instance. For this reason, *hydrochloric acid* and *hydrogen chloride* are generally used as interchangeable terms, but the former should be applied to the water solution of the gas.

The formula for hydrochloric acid will still be HCl , because the solution contains the molecules represented by HCl , but, in water, some of these become ionised.

NOTES ON HYDROGEN CHLORIDE

Hydrochloric acid has been known for a long time. In the days of the alchemists it was a constituent of *aqua regia* (see under Chlorine, page 105). Afterwards it was prepared from common salt, and known as *Spiritus Salis*; later still, Priestley investigated the properties of the gas

hydrogen chloride, and named it *Marine Salt Air*. Even at the present day the solution of the gas in water is often called *muriatic acid*, from *muria*, meaning sea salt.

The commercial acid is obtained in large quantities as a by-product in alkali manufacture, as in the preparation of sodium hydroxide and sodium carbonate from common salt. The salt is treated with sulphuric acid and the gas given off is captured and dissolved by being passed over water in large jars.

The liquid commonly called hydrochloric acid is a solution of hydrogen chloride in water. The gas is very soluble, thus water at 0° C. and at a pressure of one atmosphere will dissolve about 500 times its own volume of hydrogen chloride to form a yellow liquid of specific gravity 1.2, containing about 40 per cent. of gas, by weight. The commercial acid has a strength of 25-30 per cent. of gas, by weight, dissolved in water.

CHAPTER XXXI

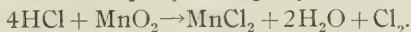
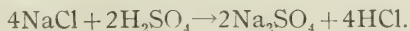
CHLORINE

We have already found that if hydrochloric acid be brought into contact with a metal like magnesium or zinc, a reaction will occur in which the hydrogen of the acid will be replaced by the metal. Experiment 82 shows that in a somewhat similar way certain oxidising agents have the power of replacing the chlorine with oxygen. This is generally expressed by saying that the hydrogen of the acid becomes oxidised to water and the chlorine is either set free, or enters into combination with another element present. Thus the reaction between manganese dioxide and hydrochloric acid is represented by the equation: $4\text{HCl} + \text{MnO}_2 = 2\text{H}_2\text{O} + \text{MnCl}_2 + \text{Cl}_2$.

Some chlorine comes off as a free gas because, under the conditions of the experiment, manganese is a divalent element towards chlorine, but it was tetravalent towards oxygen, thus the quantity of oxygen available for combination with the hydrogen of the acid displaces twice as much chlorine as will combine with the manganese, and the excess passes off free. Commonly manganese dioxide is used as the oxidising agent, but such compounds as lead dioxide or nitric acid will serve the purpose equally well.

The hydrochloric acid required in this reaction may be produced in presence of the oxidiser, as when a chloride of one of the alkaline metals is heated with sulphuric acid and manganese dioxide. If the reactions occurred in

succession they would be indicated by the following equations:



When they occur simultaneously, the replacement of the chlorine goes farther, if excess of sulphuric acid be present, and the chloride of manganese becomes altered to the sulphate, thus: $2\text{NaCl} + 2\text{H}_2\text{SO}_4 + \text{MnO}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2$.

At the present time chlorine is formed as a by-product in the electrolytic manufacture of sodium hydroxide. (See under that heading). In this operation strong brine is electrolysed, and as the ions formed in the solution are those of sodium and chlorine, the latter substance passes off at the anode as a gas and is utilised in the manufacture of such materials as bleaching powder, or is liquefied and stored for use in industrial operations, such as the chlorination process for gold.

Chlorine is a very active substance chemically, in the sense that it combines readily with many of the elements, especially with the metals. It does not, however, unite directly with oxygen or carbon, though compounds of these elements with chlorine are known. These are obtained from other combinations or by the replacement of some element in a compound by chlorine; thus chloric acid, HClO_3 , readily breaks down into chlorine dioxide and water, and chloroform, CHCl_3 , may have the hydrogen replaced by chlorine to form CCl_4 .

Hydrochloric acid may be produced by synthesis of the elements composing it; that is, by direct union of these elements. Experiment 83 shows that the combination may be effected through the agency of either heat or light. When the union takes place through the influence of

light the rate of the reaction may vary between very wide limits; thus, in bright sunlight, the union may occur with explosive rapidity; while, if the light is very faint, the act of combination may extend over many months.

It is not necessary that there should be free hydrogen mixed with chlorine in order to have hydrogen chloride formed by the union of the two. Experiment 84 shows that chlorine will form an acid in water, especially when exposed to strong light. Now there is only chlorine and water present, and we have already seen that light affects the combination of chlorine with hydrogen; hence it is reasonable to conclude that some of the water is decomposed and that hydrochloric acid is formed. This conclusion is made more certain still by the fact that oxygen, in small quantity, is set free (see Experiment 85). The rate of this reaction too is dependent somewhat on the intensity of the light.

This replacement of oxygen in water by chlorine to form hydrochloric acid is an interesting reversal of the reaction by which oxygen replaces chlorine in the same acid, Experiment 82. Such apparently contradictory results are not at all uncommon in Chemistry. They are accounted for by the Mass Action, that is, a reaction may go in different ways dependent on the mass (concentration) of one or other of the reacting substances. We have already seen that iron will deoxidise water to produce an oxide of iron and free hydrogen, while hydrogen will take away oxygen from its combination with iron to produce water and iron. The present case is similar. When chlorine is concentrated in presence of water it will displace oxygen to form hydrochloric acid and free oxygen, while oxygen set free from manganese dioxide will displace the chlorine from that same hydrochloric acid to produce water and free chlorine. In such cases it is

not unreasonable to conclude that both reactions may go on at the same time, but that one is the more pronounced for which substances are present in greater quantity.

Chlorine is more energetic than even oxygen in combining with metals, for it will form chlorides with gold and platinum, metals that are not oxidised even by concentrated nitric acid. Nitric acid oxidises hydrochloric acid and sets chlorine free; thus, $\text{HNO}_3 + 3\text{HCl} \rightarrow 2\text{H}_2\text{O} + \text{NOCl} + \text{Cl}_2$. As the acids individually do not attack the metal, and as the compound produced is chloride of gold, the inference is reasonable that the metal and the chlorine combine. This conclusion is strengthened by the results of Experiment 89.

The mixture of nitric and hydrochloric acids is known as *aqua regia*, because the liquid "dissolved" the *noble* metals of the alchemists. It was formerly prepared by distilling nitre and salammoniac with oil of vitriol, that is, potassium nitrate and ammonium chloride with sulphuric acid.

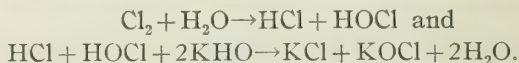
The fact that chlorine unites readily with gold to form a soluble compound is taken advantage of for the extraction of the metal from its ore, particularly in cases in which the gold is disseminated through the rock in such a way that its recovery by other processes would be difficult. The method is known as The Chlorination Process.

Chlorine has an extensive application in those industries in which it is necessary to decolourise fabrics or materials made of vegetable fibre.

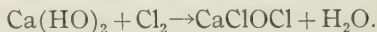
It has already been found, Experiment 84, Manual, that chlorine in presence of water will give an acid reaction after a time. The chemical action is indicated by the following equation: $2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HCl} + \text{O}_2$. Chlorine, then, in solution tends to combine with hydrogen and to set oxygen free.

Many of the dyes of commerce and the natural colouring matters of plants are very complex chemical compounds, that may either lose hydrogen through the action of the chlorine, or become oxidised by the oxygen set free in their presence by the decomposition of the hypochlorous acid. In either case the colouring matter is altered in its composition, and, therefore, becomes a different substance; and as the distinctly coloured compounds are relatively few in number, the change in composition is likely to result in a destruction of colour, or in *bleaching*. The decolourising of compounds through the action of chlorine in solution must then be accounted for by an alteration in the composition of these substances, in some cases due to withdrawal of hydrogen, in some to oxidation, and in others to both actions going on together.

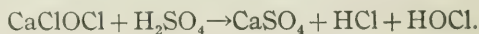
On account of the difficulty of preserving hypochlorous acid and of preparing and using chlorine as a bleaching agent, it has been found more convenient and economical to produce compounds of these substances from which they may be obtained as wanted. Chlorine passed into a solution of cold and dilute potassium hydroxide forms potassium chloride and potassium hypochlorite, thus:



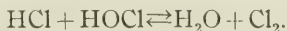
With calcium hydroxide, which sets free two hydroxyl ions from each molecule, the equation becomes



The compound $\text{CaClOC}l$ is called **Bleaching Powder**. When this is treated with dilute acid it decomposes into the calcium salt of the acid and hydrochloric and hypochlorous acids, thus:



When hydrochloric and hypochlorous acids are set free together they react to produce water and chlorine:



According to conditions, the chlorine thus formed may combine with the hydrogen of some of the water present, or with hydrogen of the colouring matter, or with both; and the oxygen set free from the water may oxidise the colouring matter, as previously mentioned.

Bleaching by chlorine is confined mostly to cotton and linen goods, as materials made of wool and silk are liable to injury by its action. It decomposes animal fibre to some extent and does not decolourise it.

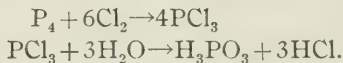
From what has been said about the decomposition of bleaching powder, it is clear that it may be employed as a convenient substance from which to prepare chlorine, especially if the presence of a little hypochlorous acid in the gas is not objectionable.

Bleaching powder is manufactured by passing chlorine into closed chambers in which calcium hydroxide (slaked lime) is spread in thin layers.

The substance commonly sold as *chloride of lime* is bleaching powder, which is largely prepared as above, from the chlorine that is obtained as a by-product in the preparation of sodium hydroxide from salt. It finds extensive use in laundries and as a disinfectant. The same properties that make it valuable for the removal of stains and colors cause it to be a serviceable agent for the removal of many ill-smelling gases and conditions that breed disease.

The experiments with chlorine, bromine, and iodine show remarkable similarities among the three elements in some particulars, and striking gradations of properties in others. In studying them, the *common* method of prep-

aration is noticeable. A general equation for the reaction that produces the free element may be written as follows: $2KR + MnO_2 + 2H_2SO_4 \rightarrow MnSO_4 + K_2SO_4 + 2H_2O + R_2$. In this R represents either chlorine, bromine or iodine. All three bleach litmus and other vegetable colouring matters. All form acids with hydrogen when they react with phosphorus and water, and when they are heated with hydrogen under proper conditions. The reaction with phosphorus and water consists in a combination of the chlorine, etc., with phosphorus, then a reaction between that compound and water, thus:



H_3PO_3 is phosphorous acid, from which the hydrochloric acid is separated by distillation. Hydrobromic and hydriodic acids are prepared in a similar way, Experiments 92, 95.

The gradation of properties is shown by bromine being intermediate to chlorine and iodine: (1) in its physical condition at ordinary temperatures; (2) in its activity as a bleaching agent; (3) in its power to displace iodine and in its being itself displaced by chlorine; (4) in the stability of its hydrogen acid, being less than that of hydrochloric but greater than that of hydriodic acid.

These three elements with fluorine are known as the halogens (sea salt formers); they make up one of the groups or families in which the elements are arranged, for convenience, on account of the similarity of their properties and compounds.

CHAPTER XXXII

CARBON

Carbon is found in all living things in union chiefly with oxygen, hydrogen and nitrogen; and it may be obtained by heating such substances out of contact with air. Wood, for instance, heated in a closed retort or kiln, parts with the volatile materials that it contains, and only those that are non-volatile at that temperature remain. This residue is wood charcoal, which is mostly carbon, but with some mineral impurities that in solution were carried into the tissues of the plants. These minerals form the ash—the incombustible material—that is left when wood or charcoal is burned. Animal charcoal, or bone black, is obtained by heating bones, blood and slaughter-house refuse in closed vessels.

The purest artificial carbon is prepared from refined cane sugar. If such substances as coal oil, illuminating gas, turpentine, or camphor be burned, and the flame cooled, or if the supply of air be insufficient, the chemical action will be incomplete, and carbon—instead of being oxidised to a gas—will pass off as a fine black powder, commonly called *soot*. This is the lampblack used by painters.

Charcoal in all its varieties is a non-crystalline substance. The different sorts of mineral coal are also largely impure forms of carbon of the non-crystalline or amorphous (formless) kind. Coal contains both mineral matters which form the ash that remains after combustion, and volatile ingredients that are set free by heat-

ing. The latter, when collected and freed from some objectionable substances, make up the *coal gas* that is used for heating and for lighting houses.

Carbon exists free in nature in two forms, both crystalline, yet differing greatly from each other as well as from amorphous carbon. These are (1) *graphite*, plumbago, or black lead, and (2) *diamond*. The former is found frequently in crystalline rocks as black shining scales, but sometimes occurs as massive deposits that are of economic value. Graphite mines are worked in Eastern Ontario and in Quebec. This form of carbon may be prepared artificially by fusing some substance rich in carbon with molten iron, and allowing both to cool slowly together. Diamonds are found in only a few places, as Borneo, Brazil, and South Africa. They are valuable on account of their hardness and brilliancy.

Charcoal, graphite and diamond, though differing so widely in some properties, are chemically the same substance, for when equal weights of them are heated in presence of oxygen they form equal weights of carbon dioxide, and nothing else. Because of this identity of substance and the difference in their physical properties, as hardness, transparency and crystalline structure, they are often referred to as *allotropic* forms of carbon. (Allotropic means turned into another.) The terms allotropic, allotropism, and allotropy, are not of much descriptive value, however, because they lack definiteness of meaning. Some other elements, notably sulphur, oxygen and phosphorus, also exist in different forms. These forms are probably due to variations in the minute structure of the substance. We know, for instance, that ordinary oxygen exists in a molecular state that is represented by the symbol O_2 . This means that the unit masses of this element, set free separately in chemical

action, unite in twos to form the substance called oxygen. But ozone, which is chemically the same as oxygen—because it forms the same chemical compounds—shows different physical properties, and consists of molecules represented by O_3 . Whether the substance exists as oxygen or ozone, depends on whether the atoms when set free group themselves in twos or in threes. This change in grouping is accompanied by a very considerable change of energy, as shown by the character and rate of their reactions with other substances.

It is likely that the forms of carbon, and of other elements described as allotropic, owe their differences either to different atomic groupings in the molecules, as in the case of oxygen and ozone, or to an arrangement of the molecules themselves in definite groups peculiar to each form of the substance. In any case, the atoms in the molecule of charcoal may be made to enter into combination with oxygen at a much lower temperature than that required to bring about a similar combination when graphite is the form of carbon used; this would seem to indicate a different grouping of the atoms in the two substances, graphite and charcoal.

Many minerals and rocks have carbon as one of their components. The various kinds of limestone and dolomite, the ore of iron called siderite, and the carbonates of copper, lead and zinc are examples. Natural gas and mineral oils, like petroleum, are very largely composed of compounds of carbon and hydrogen. In the plant world such substances as the resinous secretions of the conifers, amber, camphor and the vegetable oils, all have much carbon in their composition, while woody tissue is largely composed of that element.

Uses of Carbon.—Amorphous carbon, and substances rich in that element, that are easily decomposed, furnish

a very large part of the heat and light used for domestic and industrial purposes. Wood charcoal is used as a heating agent, and in filters as an absorbent for gases. On account of its extreme porosity it exposes a very large surface area to the gas in which it is immersed, and it is believed that there is a condensation of the gas within the pores, for the volume absorbed is, in some cases at least, very much larger than that of the charcoal itself, as in Experiment 100. Lampblack is employed as a painters' colour, and as the material out of which printers' ink is made. Graphite ground and made into a paste with clay forms the "lead" out of which "lead pencils" are made. On account of its ability to withstand high temperatures, graphite is mixed with fire clay and made into crucibles for use in furnaces. It is employed as a polishing material for iron, and as a conductor of electricity under circumstances which render metals unsuitable for that purpose. It is extensively employed as a lubricant for machinery either where high temperature prevents the use of oil, or the friction of heavy parts requires a material more resistant to pressure and wear than oil is.

When coal is heated in closed retorts to drive off the volatile materials that make up illuminating gas, there is left on the sides of the retort a coating of amorphous carbon that is hard and very pure. It is made into plates for electric batteries, pencils for arc lamps and brushes for dynamos. The carbon filaments of incandescent lamps are made of wood charcoal, and are prepared by heating fibres of bamboo under conditions which prevent combustion.

Coke which is obtained by heating certain kinds of soft coal, out of contact with air, contains the "fixed" carbon and mineral matters of the coal, that is, the substances that are non-volatile at a red heat. It is a hard,

grey, very porous solid, that in cooling cracks and opens into prismatic blocks. It is extensively used as a fuel, especially in smelting operations, for which it is more suitable than coal, partly because it is relatively free from injurious volatile ingredients, such as sulphur; partly on account of its hardness and the resistance which it offers to the crushing force which would grind coal to powder, thus stopping the passage of gases; partly on account of the intense heat it produces because of its open structure, which permits rapid oxidation.

The following is a tabulated view of the forms of carbon to which reference has been made:

Amorphous	{	artificially prepared	{	Charcoal
				Lampblack
				Boneblack
				Gas Carbon
				Coke
	{	naturally occurring	{	Coals of various kinds con- taining mineral and volatile impurities.
Crystalline, naturally occurring				{
				Graphite
				Diamond.

CHAPTER XXXIII

OXIDES OF CARBON

Among the elements, carbon is that one which enters into the greatest number of combinations; so numerous, indeed, are these compounds that the chemistry of carbon has become a branch of the science by itself, with methods of investigation and a literature of its own. It will be possible at this stage, therefore, to refer to only a few of these compounds whose chemical relations or industrial applications mark them as specially important.

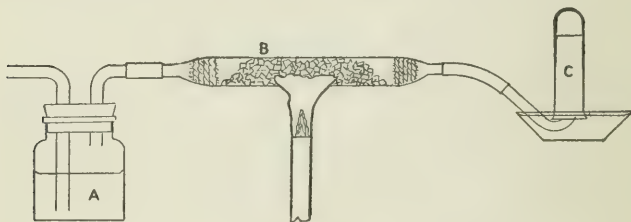


FIG. 6

Oxides of Carbon.—EXPERIMENT IV. B is a hard glass tube about half an inch in diameter, one end is drawn out to half that size, a loose plug of asbestos is put in, then about three inches of the tube loosely filled with broken charcoal, a plug of asbestos inserted behind it, and the other end drawn out. A is a bottle containing a little water, and C is a test tube or bottle filled with caustic soda solution over a vessel of the same liquid. The apparatus is connected as shown, the tube at the left being attached to a supply of oxygen.

When the charcoal is heated to redness pass oxygen *very slowly* over it. The bottle A will show how fast the gas is entering B; a small bubble every two or three seconds will be sufficient. After the air has been swept out of B, place the receiver C over the delivery tube and collect the gas that escapes from B. When C is full let it stand over the soda solution for half an hour, then test the remaining gas with lime water. Bring a lighted match to the mouth of the vessel C; then shake the contents with lime water.

What substances were present in B? What three substances could possibly have passed out of B? What chemical action goes on when substances burn in air? What is known about the proportion of oxygen in combination in the gas in C before it burned, as compared with that in it after the combustion?

Repeat the experiment, but pass the oxygen more rapidly, two or three times as fast as in the former case.

What differences in result are there now as compared with those formerly noticed?

Carbon dioxide is the highest oxidation product of carbon known; and the experiment just made, with Nos. 101, 102, demonstrate the possibility of producing the dioxide from carbon, either by one stage of oxidation, or by two. It is evident that a compound of oxygen and carbon first entered the vessel C, and that gas combined with more oxygen to produce the dioxide. It is equally evident that when carbon is burned in a free supply of oxygen the higher oxide is formed at once.

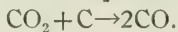
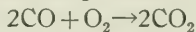
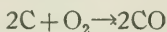
The colourless gas that was collected in C, and burned to carbon dioxide, was *carbon monoxide*, CO.

EXPERIMENT V. Use the apparatus and materials of the last experiment, but substitute for the oxygen carbon

dioxide (see Experiment 103). Pass the gas *very slowly* over the red-hot charcoal. Test the gas that comes off with a lighted splinter, then pour lime water into the receiver C.

What gas entered the tube containing the charcoal? What gas passed out of it? What oxidation and what reduction took place during this operation?

The above series of reactions between oxygen and carbon may be represented by the following equations:



The reaction, therefore, which occurs with carbon monoxide and oxygen is reversed when carbon and the dioxide are heated together. Not only that, but the products of the reaction are dependent on the masses of the reacting substances. Carbon heated in presence of a limited supply of oxygen forms the monoxide, but with plenty of oxygen the dioxide is produced. That is, whether the lower oxide or the higher one is formed is dependent on whether the supply of oxygen is diffused or concentrated; in other words, on the mass per unit volume. It is evident that greater concentration will cause greater quantities of reacting substances to come into contact in a given time, with the result that both the rate and the product of a reaction may be altered, as in the case of carbon and oxygen. In the reversed action the oxygen is swept out of the tube by the carbon dioxide, and the concentration of carbon in presence of this gas results in a rearrangement of the constituents of the molecules in such a way as to permit the oxidation of the greatest quantity of carbon possible; hence, the formation of the monoxide by reduction.

Carbon Monoxide.—Carbon monoxide is a colourless combustible gas that is actively poisonous when inhaled. It burns with a characteristic blue flame that may often be seen over a coal fire, especially if fresh fuel has just been put on. In this case the gas is produced partly by the reduction of carbon dioxide that was formed in the lower part of the fire and reduced by passing through the hot coals, partly by the rapid combustion of the finer particles of the fresh coal with a limited supply of oxygen. Carbon monoxide is a valuable heating agent when burned, so that any of it that is allowed to escape unconsumed, among furnace gases, is a direct loss. It is formed in large quantities in most cases in which coal is burned; and is one of the by-products in such operations as the reduction of ores by coal. In the smelting of iron, for instance, the ore, as iron oxide, is mixed with coke and limestone, and charged into the blast furnace (smelter), which contains a mass of ignited coke. The burning coke is supplied with oxygen partly by hot air driven in through pipes, partly by reducing the oxide of

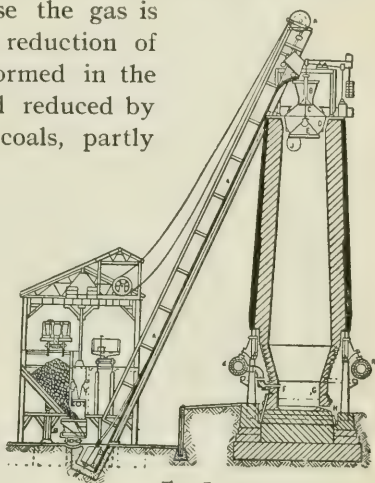


FIG. 7

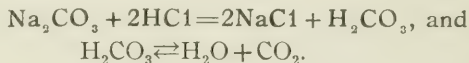
(The figure is a diagram of an iron smelter)

The material is drawn up the incline A, and tilted into the hopper B. The cone C opens and the contents of B drop into the second hopper D; from there they are dropped into the furnace. The two cones prevent the escape of much gas when charging. J is a pipe carrying off gas formed in the furnace, which is about 20 per cent. carbon monoxide and is used for heating. K is a pipe leading round the furnace, carrying air heated to 600°-800°, which is fed into the furnace through branches, F, called tuyeres. H is the vent through which the molten metal runs out, and G is the pipe to carry off slag.

iron. One product of the combustion is carbon monoxide, which is collected at the furnace mouth, led away and burned to heat the air of the blast, and to drive the machinery of the mills. This gas is also one of the necessary ingredients of "Water Gas" and "Producer Gas," to which reference will be made later.

Carbon Dioxide.—Carbon dioxide is the most abundant product of fuel combustion; and from this source it passes into the atmosphere to be dissolved by water or absorbed by plants. Animals, too, exhale the gas as one of the waste products of their bodies, and it is set free by decaying vegetation and by the decomposition of some rocks, chiefly limestones.

The gas is formed when carbonaceous matters are burned, but that is not a suitable method of preparation if it is wanted either for laboratory or industrial purposes, because of the other substances that would be mixed with it, such as carbon monoxide, and nitrogen if the combustion took place in air. There is a large class of salts, known as carbonates, which are formed by the interaction of carbonic acid, H_2CO_3 , and a base. It is an important property of these salts that they react with the common acids to set carbonic acid free, but the latter compound exists only in solution, and even then to a limited extent, as it undergoes decomposition into water and carbon dioxide when separated from the solvent. As an illustration, sodium carbonate reacts as follows with hydrochloric acid:

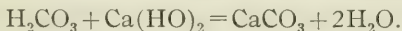


Limestone is a naturally occurring carbonate of calcium that, in its crystalline state, as marble or calcite, is quite free from the clay and other impurities that are

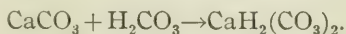
found in the bedded rock. On account of its cheapness, and the ease with which it may be obtained, marble is the common source of carbon dioxide for laboratory purposes.

Some properties of the gas have been learned from the experiments; for example, its appearance, weight, solubility, and failure to either burn or support combustion. In solution it forms a very weak acid, that is, an acid which is only slightly ionised. The salts, however, which result from its union with bases are quite stable, and are highly ionised in solution, so that it must not be assumed that the salts are easily decomposed because the acid does not act energetically.

The presence of carbon dioxide is indicated by the formation with lime water of a white solid, as a very fine powder. Lime is calcium oxide, CaO , and this when dissolved in water becomes the hydroxide, $\text{Ca}(\text{HO})_2$, thus $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{HO})_2$. The latter substance is popularly known as slaked lime, and is slightly soluble in water. It is a rather strong base and reacts with carbonic acid to produce calcium carbonate, which remains suspended for some time as a fine white powder in the liquid, thus producing the milky appearance.



Calcium carbonate is insoluble in water alone, but it is dissolved to some extent by a solution of carbonic acid, that is, by water holding carbon dioxide in solution. This is accounted for on the theory that calcium carbonate will combine with carbonic acid to form a compound represented by $\text{CaH}_2(\text{CO}_3)_2$, and this acid carbonate of calcium, is soluble.



This in itself is a matter of no particular importance, but in two respects it produces results that are note-

worthy. Wherever limestone is exposed to the action of rain water that has dissolved carbon dioxide from the air, or of earth waters that have dissolved the same gas from decomposing substances, this limestone gradually wastes away (weathers), going into solution. The material thus carried away has often been deposited in other forms and other places. Caves and water channels in limestones, calcite in veins, stalactites and deposition of limestone about springs, may generally be traced to the chemical action described above. Steam boilers are liable to become coated with a lining of non-metallic sediment, especially when hard water is used in them. This "fur," as it is called, consists, in the first case, of compounds of calcium or magnesium that were dissolved in the water, and through boiling were thrown out of solution. (See Experiment 106.) When calcium carbonate is dissolved in water it is held in solution by the agency of carbon dioxide that is also dissolved; boiling the water drives off the dioxide and the carbonate is thrown down as a precipitate. This precipitation, mainly of carbonates and sulphates of calcium and magnesium, is a cause of great expense to steam users, because it interferes with the efficiency of the boilers. It causes an increased consumption of fuel, and an outlay for the removal of the coating. A tea-kettle that has been in use for some time will furnish an illustration of this deposition of solid material.

Uses of Carbon Dioxide.—A soda water fountain is a contrivance for generating carbon dioxide and keeping it under high pressure in the presence of water. When the pressure is removed, as when the liquid is drawn off through a tap, the dissolved gas volatilises in part, but the liquid is still a solution of carbonic acid. The substances, called *aërated* waters, are, in general, solutions

of carbon dioxide in water that contains flavouring materials.

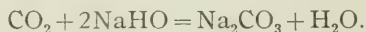
When calcium carbonate, as limestone, is heated sufficiently, it becomes decomposed into calcium oxide (lime) and carbon dioxide. If the lime thus produced be exposed to the air, it will gradually revert to the carbonate by action of the carbonic acid formed from the moisture and carbon dioxide in the air. This product is air-slaked lime. If the lime be mixed with water, as when it is made into mortar, this chemical action will be hastened, and the hardening of mortar, apart from the mere drying process caused by evaporation, is due to an alteration of calcium hydroxide (slaked lime) into the carbonate, $\text{CaO} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$.

Baking powders are mixtures of ingredients so arranged that, under suitable conditions of moisture and heat, carbon dioxide will be set free, and the gas thus generated is used as a means of preventing the glutinous mass of flour and water from becoming too compact for food material.

Plants obtain the carbon necessary for their growth from the carbon dioxide of the air. This compound is absorbed by the leaves, and, in the presence of sunlight, is decomposed by the green colouring matter of the cells, being thus changed, by combination with oxygen and hydrogen, into carbohydrates, or compounds composed of carbon, oxygen, and hydrogen, the latter two in the proportions found in water. Starch, $\text{C}_6\text{H}_{10}\text{O}_5$, and cane sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, are two common examples of these substances. It thus happens that plants are directly, and animals are indirectly, dependent on carbon dioxide for their supplies of food material.

Experiments 99 and 101 show the effect of sulphuric acid on substances that readily part with hydrogen and

oxygen in the proportions necessary to form water. Wood is mostly cellulose, which has a composition somewhat similar to that of starch, $C_6H_{10}O_5$. Sulphuric acid tends to combine with water to such an extent that it will cause the decomposition of many substances by the withdrawal of the hydrogen and oxygen to produce water. It will be noticed that in wood, if the material for five molecules of water be withdrawn from one molecule of cellulose, only carbon will be left; and in the case of sugar, $C_{12}H_{22}O_{11}$, eleven molecules of water may be similarly removed from one molecule of the original compound. Oxalic acid is $H_2C_2O_4$, and when a molecule of water is withdrawn, there is left C_2O_3 , or rather a mixture of CO and CO_2 , the latter may be absorbed by sodium hydroxide solution.



When oxalic acid is treated with sulphuric acid, and the gases that come off are passed slowly through any strongly alkaline solution, carbon monoxide alone will pass out, and may be collected. The removal of carbon dioxide from a mixture of gases of which it is one, is dependent on its union with water to form an acid, and the reaction of that acid with the base present to form a salt.

Ventilation.—Under normal conditions there is about one volume of carbon dioxide in every 2500 of air, but expired air contains about four per cent. of this gas. Since an adult person exhales about 20 litres per hour of carbon dioxide, it is clear that air breathed repeatedly in a closed room will soon become overloaded with the dioxide. One-tenth of one per cent. is generally set as the maximum limit that this gas can reach in living rooms without producing injurious effects. These effects, however, are probably not due to the dioxide itself, so much

as to other impurities that accompany it, and that accumulate in about the same proportion in which it does. The quantity of carbon dioxide in the air of living rooms is therefore taken as an indication of the degree of vitiation which that air has reached. In order to prevent ill results from repeated respiration of the same materials a circulation must be established by which fresh portions of air will enter the room, and that impaired for breathing purposes will be swept out. This replacement constitutes *ventilation*.

PROBLEMS

1. Chemical Fire Extinguishers are charged with carbonate of sodium and sulphuric acid. Explain (1) how the material is formed that extinguishes the fire; (2) why the fire is extinguished. Refer to any experiment that confirms the explanation.

2. Assuming that coal is 75 per cent. carbon and that this burns to the dioxide, find what relation there is between the weight of the coal and the weight of the gas produced.

3. Mix a little red lead with powdered charcoal and heat the mixture in a hard glass test tube. After the powder has been red-hot for five minutes pour it out on a plate, wash away the charcoal, and examine the metallic substance left. Given that red lead has the composition Pb_3O_4 , write an equation for the chemical action that probably resulted in the reduction.

4. Good anthracite coal is about 92% carbon, 12 grams of carbon burn to 44 grams of carbon dioxide and evolve 96,900 calories of heat. If a kilogram is equal to 2.2 lbs., how much water should be changed into steam by the combustion of 1 lb. of coal, the water at 50° C., latent heat of vapourisation 537?

5. Read about the formation of coal and write a note on the relation of coal supply to industries, including metallurgy, steam production and transportation.

6. Why does water thrown on burning wood put the fire out?

CHAPTER XXXIV

CARBIDES

Carbon is rather an inactive substance chemically, because it enters into combination directly with but few other elements, and with some of these only at the excessively high temperature of the electric furnace. Two of the compounds, however, that carbon does form, even at a moderate degree of heat, have been closely related with the progress and civilisation of mankind. The use of fuels as a source of heat for domestic and industrial purposes is chiefly dependent on the tendency of carbon to unite readily with oxygen; and, in doing so, to set free heat-energy enough to make the chemical action continuous and to raise the temperature of surrounding bodies. To realise just what we owe to this one kind of reaction, it is only necessary to think what would happen if coal were to cease to burn for a single day. Iron, too, will combine with carbon at a temperature below red heat to form a carbide, Fe_3C . This carbide is soluble in molten iron and the quantity dissolved determines mostly the kind of iron produced. A steel, for instance, that contains one and a half per cent. of carbon has dissolved in it twenty-two and a half per cent. of the carbide; and it is the dissolved carbide that gives this steel its special qualities.

Since the electric furnace became a means for the production of materials of commerce, two other carbides that have an industrial value have been manufactured. These are the carbides of calcium, CaC_2 , and of silicon, SiC . The

former is made by heating in an electric furnace a mixture of lime and coke; and the latter by similar treatment of sand or ground quartz and coke. The calcium carbide is the material from which acetylene, an exceptionally

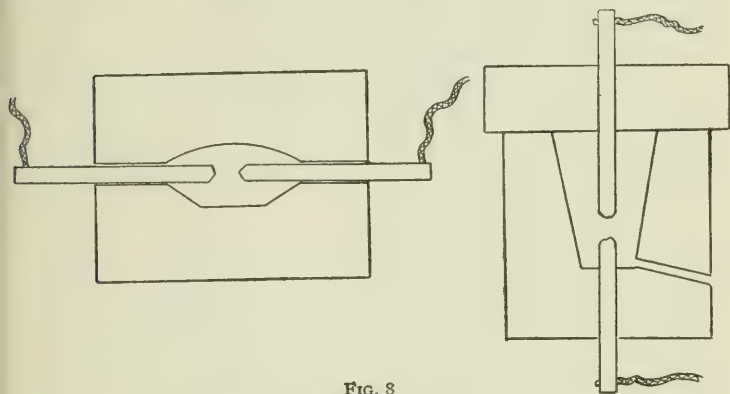


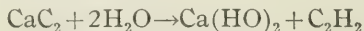
FIG. 8
Diagrams of Simple Electric Furnaces

brilliant illuminant, is prepared. The silicon carbide, known commercially as carborundum, is, next to the diamond, the hardest substance known; so it is used extensively as an abrasive in grinding and polishing metals, and as a material out of which an especially resistant fire brick is manufactured.

CHAPTER XXXV

ACETYLENE

Acetylene will serve as an example of a hydride of carbon, or of a hydrocarbon as the term is generally used. It is easily prepared by causing calcium carbide to come into contact with water, then the two react to produce acetylene and slaked lime.



When properly supplied with oxygen the gas burns with a very luminous white flame. Acetylene, when burning, evidently undergoes decomposition, because a large quantity of carbon is set free, as shown by the *soot* or *smoke* when the gas is ignited in quantity. Acetylene is highly explosive when mixed with air in proportions ranging from 3% to 83%, and, if it is subjected to pressure, it sometimes dissociates with great violence. On account of its high luminosity, when ignited at suitably-made burners, the gas is frequently used as an illuminant. There have been destructive explosions caused either by its careless handling, or by faulty appliances allowing air to become mixed with acetylene. In such cases the flame at the burner is liable to run back through the connecting tubes and ignite the mixture in the receptacle. Compare Experiment 112.

Another hydrocarbon of some importance is *methane*, CH_4 , popularly known as *Marsh Gas*; and in coal mining regions, it is *Fire Damp*. It is produced by decaying vegetable matters and exists quite frequently in pockets

and crevices in coal seams. As these are opened the gas escapes into the air in the galleries and workings, and a violently explosive mixture is thus produced, which a naked light on a miner's cap may ignite. As a precaution miners are compelled to use lamps protected with wire gauze, known as Safety Lamps. The gauze prevents the flame within the enclosure from igniting the inflammable gas outside, see Experiment 117.

CHAPTER XXXVI

LAW OF MULTIPLE PROPORTIONS

Carbon combines with oxygen to form two compounds, the monoxide and the dioxide. Sulphur forms the dioxide, SO_2 , and the trioxide, SO_3 . Nitrogen forms compounds represented by the formulæ N_2O , NO , N_2O_3 , NO_2 or N_2O_4 , N_2O_5 . Similarly iron may unite with oxygen to produce FeO , Fe_2O_3 , Fe_3O_4 , and with chlorine to form FeCl_2 and FeCl_3 .

The Law of Definite Proportions, however, makes it clear that if two elements combine they do so in quantities either proportional to their atomic weights or to simple multiples of those weights. The atom of carbon weighs 12; that is, the unit mass of carbon taking part in chemical action is 12 times as great as the unit mass of hydrogen. Similarly the atom of oxygen weighs 16. It follows then that 12 parts by weight of carbon combine with 16 of oxygen, or some simple multiples of these quantities enter into union, but not necessarily the same multiple of each unit mass. Analysis of the oxides of carbon show that 12 parts by weight of carbon unite respectively with 16 and 32 of oxygen. In the same way 28 parts by weight of nitrogen may combine with 16, 32, 48, 64 or 80, (that is one, two, three, four, or five times sixteen) parts of oxygen. Six times the atomic weight of iron unites with six or nine or eight times the atomic weight of oxygen. One atomic weight of sulphur unites with two or with three atomic weights of oxygen. These relationships are summed up in the Law of Multiple Proportions, as fol-

laws: If two substances form more than one compound, and if the weight of one of them be constant, the weights of the other will be in a simple ratio to one another. That means if two substances, M and N, unite to form more than one compound, the portions by weight of M that combine with a fixed quantity of N are related to one another in the proportions of small whole numbers.

CHAPTER XXXVII

AVOGADRO'S HYPOTHESIS

The behaviour of gases under the influence of changes of temperature has been carefully investigated, and the result is stated as follows in the Law of Gay-Lussac and Charles: All gases under constant pressure vary in volume directly as their absolute temperature. This means that regardless of their nature, whether light or heavy, simple or compound, pure or mixed, all gases change equally in volume when heated or cooled equally.

The effect of heat energy on a gas is shown by the pressure, or expansive force exerted by the gas on the walls of the containing vessel. This force is believed to be due to the impacts of the molecules of the gas on the walls, and its intensity is measured by the number of impacts per second on each unit of wall surface. Since equal changes of temperature produce equal effects in all gases, it follows that all kinds of gases under similar conditions must cause equal numbers of molecular impacts per second on unit surface of the containing vessel. This evidently can be true only if equal volumes of all gases contain equal numbers of molecules.

Again, the most careful study of the effects of pressure on all kinds of gases gives the result stated in the Law of Boyle and Mariotte—all gases under constant temperature vary in volume inversely as the pressure upon them. But pressure, like heat, is a form of energy and does work upon the gas. This work is evidently expended in over-

coming the internal molecular energy of gases, which causes the molecules to diffuse or separate. Since equal pressure produces equal effects upon equal volumes of all gases, it is clear that this intermolecular repulsion is equal among all gases at the same temperature and pressure. This can be true only if the molecules of all gases are similarly situated with respect to one another, that is, are kept at equal distances from each other by equal forces. So it seems fair to conclude that under similar conditions a molecule of one kind of gas occupies the same space as a molecule of another kind, or that in equal spaces there are equal numbers of molecules. This is the same conclusion as that reached from the consideration of the effect of heat. It was stated in the following way, in 1811, by Avogadro, an Italian physicist: *Equal volumes of all gases, at the same temperature and pressure, contain equal numbers of molecules,*

SOME APPLICATIONS OF AVOGADRO'S HYPOTHESIS

Molecules of all gaseous elements consist of 2 atoms

It has been said (page 77) that the molecules of hydrogen, oxygen, nitrogen, and chlorine, are represented, respectively, by the symbols H_2 , O_2 , N_2 and Cl_2 , and that no such substance as that represented by H, O, N, or Cl has a free existence. The latter symbols represent atoms of the elements. The gaseous elements, however, do not exist as atoms, but as molecules.

The reasons for the last statement, and the one that asserts that the molecule of hydrogen is H_2 , can now be given.

In the synthesis of hydrogen chloride, that is, in forming the compound by causing the elements to unite, one

volume of hydrogen combines with one volume of chlorine to produce two volumes of the chloride. One volume of the compound must be made from half a volume of hydrogen and half a volume of chlorine. Since *equal volumes of gases contain equal numbers of molecules*, if the volume be continually reduced we will finally arrive at the molecule as the unit of volume of a free gas. One volume of hydrogen chloride is formed by the union of half a volume of hydrogen with half a volume of chlorine. The molecule of hydrogen chloride, the smallest part of the substance that can have free existence, must be composed of hydrogen and chlorine, so cannot be either elementary or monatomic; and since hydrogen and chlorine enter into the composition of the compound in equal volumes, the molecule of the chloride is made up of half a molecule of each constituent. It therefore follows that the molecule of hydrogen is capable of being divided into two similar parts, and so is the molecule of chlorine. These half molecules are the smallest parts of the elements entering into any chemical action, as far as known, and they are, therefore, believed to be the portions formerly referred to as atoms, and represented by the symbols H and Cl; consequently the molecular symbols of these elements are written H_2 and Cl_2 .

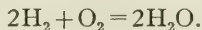
Again from the experimental fact that two volumes of hydrogen unite with one volume of oxygen to produce two volumes of water, as gas, it may be shown that the oxygen molecule is divisible into two equal parts; but no known compound calls for its division into more than two parts, hence the symbol for oxygen gas is O_2 .

Nitric oxide can be shown by experiment, to be composed of equal volumes of oxygen and nitrogen; and one volume of each produces two volumes of the compound when they unite. The molecule NO, therefore, is com-

posed of half a molecule of nitrogen and half a molecule of oxygen, so that the nitrogen molecule must also be represented by N_2 .

II

By the use of Avogadro's Hypothesis we are enabled to calculate volume relations among reacting substances that are gaseous. For instance, we represent the combination of hydrogen with oxygen by the equation



Two molecules of hydrogen unite with one of oxygen to form two molecules of water. If we assume that there are x molecules of oxygen in a volume, then x times two molecules of hydrogen combine with x molecules of oxygen to produce x times two molecules of water; or two volumes of hydrogen combine with one volume of oxygen to produce two volumes of water, provided the latter substance be kept as a gas. This may be experimentally shown in the case of oxygen and hydrogen by immersing the eudiometer in vapour that is kept at a temperature above 100° C., then causing the hydrogen and oxygen in it to unite. The volume relation of the substances reacting is the same as the molecular one.

The combustion of carbon monoxide shows an exactly similar result, thus: $2CO + O_2 = 2CO_2$. Two molecules of the monoxide with one molecule of oxygen produce two molecules of the dioxide, hence two volumes of the monoxide with one volume of oxygen form two volumes of the dioxide. This may be easily demonstrated by igniting measured volumes of the carbon monoxide and oxygen over mercury.

gram-molecule of ammonia - 17 gr.
density = the mass of unit volume of a substance
usually ^{III} 1 cu. cm.

A gram-molecule of any gas, at standard temperature and pressure, occupies 22.4 litres. By actual experiment, one litre of oxygen weighs 1.429 grams, at 0° C. and 760 m.m., hence 32 grams occupy 22.4 litres. Since equal volumes of gases, under like conditions, contain equal numbers of molecules, it follows that equal volumes of gases have weights proportional to the molecular weights of the substances. For instance, carbon monoxide has the molecular weight 28 and carbon dioxide, 44. If any number of molecules of the former gas be taken and the same number of the latter one, the weights of the masses will be in the proportion of 28 to 44, therefore equal volumes of these gases have weights in proportion of 28 to 44. Since by experiment 32 grams of oxygen occupy 22.4 litres, 28 grams of carbon monoxide, 44 grams of carbon dioxide, 36.5 grams of hydrogen chloride, all occupy the same volume, 22.4 litres. Further, the gram-molecule of any gas contains the same number of molecules as does the gram-molecule of oxygen, hence it occupies 22.4 litres.

IV

The density of gas at standard temperature and pressure is expressed by a number equal to one-half its molecular weight, when hydrogen is the standard for density, ($H = 1$.)

The density of any kind of matter is a ratio between its mass per unit volume and the mass per unit volume of a standard substance. 22.4 litres of hydrogen weigh 2 grams, 22.4 litres of another gas weigh x grams, then the density of that other gas is $\frac{x}{2}$. But x must be the

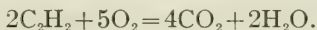
molecular weight of that other gas, hence its density is one-half its molecular weight.

In general the molecular weight of any gas is the sum of the weights of the atoms composing the molecule; the molecular weight of hydrogen is therefore 2; hence, for any gas, the density is the sum of the atomic weights of a molecule divided by 2, when $H=1$, that is when hydrogen is the standard.

Generally in engineering work, and often in physics, density is referred to air as a standard. It is worth noting, therefore, that the density of air, as referred to hydrogen, is 14.39 approximately, for one litre of hydrogen weighs 0.089873 grams and a litre of air weighs 1.2939 grams.

PROBLEMS

1. Assuming that the following equation expresses the reaction when acetylene burns, find how many litres of oxygen would be required for the combustion of 22.4 litres of acetylene, and how many litres of carbon dioxide would be produced.



2. Show that the gram-molecular weight of any gas divided by the gram-molecular weight of hydrogen expresses the density of that gas ($H=1$).

3. The composition of marsh gas is expressed by the formula CH_4 . What is its density, $H=1$? What volume would 64 grams of it occupy at standard? What would 11.2 litres of it weigh? Assuming that this gas burns to carbon dioxide and water, how would the volume of oxygen required for the combustion compare with the volume of the CH_4 ? How much carbon dioxide would be produced as compared with the volume of marsh gas burned?

4. Given that the density of air is 14.39, show that the density of carbon dioxide is nearly 1.5, $air=1$; also show that the density of carbon monoxide is the same as that of nitrogen, and the density of hydrogen sulphide, H_2S , is double that of ammonia.

5. A certain oxide of nitrogen is known to be composed of one volume of nitrogen combined with two of oxygen, so that its formula may be NO_2 , N_2O_4 , N_3O_6 , or N_4O_8 ; its density is found to be 23; which formula should be chosen for it?

6. A certain volume of carbon dioxide is passed slowly over red-hot carbon (and becomes changed to carbon monoxide); Determine if the volume of gas will be altered during the reaction; and, if so, to what extent.

7. Ammonia gas, when subjected to the heating effects of electric sparks of high tension, gradually becomes decomposed according to the equation $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$. If 10 c.c.'s of ammonia were passed into a eudiometer over mercury, and sparks of the proper kind passed between the points until no further change occurred, where would the mercury then stand in the eudiometer?

8. Remembering that a gram-molecule of oxygen occupies 22.4 litres, what volume would 3, 7, 12, 16 and 20 grams of the gas respectively occupy? What would be the weight of 1,000, 11,200 and 16,000 c.c.'s of oxygen all at standard?

XXXVIII

FLAME

Flame is usually defined as a mass of incandescent gas. The incandescence may be due either to heat applied externally, as when air is passed slowly through a tube set in a furnace, or to heat generated internally in the mass by those chemical actions known as combustion. We are concerned here only with flames of the latter class.

The burning of a candle, while a common enough phenomenon, is in reality a very complex process. First, the wax must be melted to form a pool of liquid about the wick; then this liquid, by capillary attraction, is drawn upward and vapourised by the heat. Next a series of chemical actions occurs, these consisting, in part, of decompositions, in part of combinations; but they end in the formation of carbon dioxide and water. The interpretation of the marks on the paper, Experiments 113, 114, Manual, will throw some light on the structure and chemistry of such a flame.

The wax composing the candle is a compound, or a mixture of compounds, of carbon and hydrogen. The blue cup that forms the lower part of the flame, and extends a varying distance up the sides, is made up of burning carbon monoxide. A cold bottle inverted over the flame, but not touching it, will have water, as mist, con-



FIG. 9

densed on it; and if the contents of the bottle be then shaken with lime water, the presence of carbon dioxide will be shown. We know that there is a great deal of free carbon in the flame, because it can be separated and taken out by any cold body held in the burning gas. It is clear then that there are present carbon, carbon monoxide, carbon dioxide, hydrogen, water, and one or more hydrocarbons.

The exploration of the flame with the paper gives the following information: In the lower half of the flame the burning takes place on the outside, and the central part is at a comparatively low temperature; as the paper is moved upward the combustion extends inward, so that a place is reached at which the charred ring is replaced by a disk, and that condition continues to the very top. Further, the paper strip held across the flame at the lowest position showed no free carbon, or almost none, and very little light came from that region. Higher up the carbon increased, but it too formed a ring on the paper, which gradually grew greater in density and breadth until it covered the space within the flame, and formed a fringe extending beyond the edge of the flame on the paper. This kind of carbon spot is found at all places from there to the top of the burning mass.

The flame at the bottom is practically non-luminous, and the luminosity appears to be greatest in those parts in which there is most free carbon; but if the flame be cooled by thrusting wire gauze into it the luminosity is diminished and free carbon passes off. We seem, therefore, to have the following information regarding a candle flame: (1) It is composed of gas undergoing oxidation; (2) This gas is formed by the vapourisation of the materials of the candle; (3) There is in the middle of the mass a quantity of unburning gas that is being fed from the

wick, and that is being distributed to the outer portions of the flame to take the place of the gas that has burned there; (4) The lower part of the flame is burning carbon monoxide; (5) The gas in the flame becomes in part, at least, decomposed into carbon and hydrogen; (6) There is in the upper central part a partial combustion going on which heats the solid carbon to whiteness; (7) The luminosity is connected with the free carbon; (8) There is an outside, almost invisible mantle in which carbon is being completely burned; (9) The final products of combustion are carbon dioxide and water.

The structure of a gas flame in a Bunsen burner resembles that of a candle, but it has been more fully investigated. For instance, in the case of the candle the composition of the luminous part, between the dark mass around the wick and the outer, almost invisible mantle, is not known; but in the gas flame this is found to consist of carbon monoxide and hydrogen, and the blue central cone in the non-luminous flame is burning carbon monoxide.

The luminosity of a flame may depend upon any one or more of several conditions. The most general and most important of these is the presence of solid matter heated to incandescence, and usually in a very finely divided state. On this account the substances that are burned to produce light are generally compounds that undergo easy decomposition and yield solid carbon as one of the products; the carbon thus formed exists as very fine particles suspended in the gaseous substances. The burning gases heat these particles to whiteness while they are passing through the middle portions of the flame where there is but little oxygen to burn them. The most rapid and complete combustion in such a flame takes place in the outside mantle, from which very little light comes.

The density of the burning gases and also the temperature appear to affect the luminosity. The fact that a non-luminous flame becomes light-giving when steam is passed into it is probably due to the cooling of the burning gas, and thus changing either the rate or the character of the reaction. The percentage of carbon in the burning gas also affects the quantity of light given off. Burning alcohol, C_2H_6O , gives a nearly non-luminous flame, but if a little spirits of turpentine, $C_{10}H_{16}$, be added

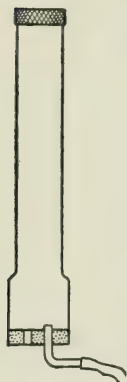


FIG. 10

to the liquid, there is a marked increase in the quantity of light emitted. The non-luminous blue flame of a Bunsen burner is produced by the combustion of a mixture of air and gas. The lack of light appears to arise from the rapid combustion and high temperature due to oxygen being distributed throughout the combustible gas. By altering the quantity of air admitted below, the character of the flame may be changed through all phases from brightly luminous to the explosive condition which causes it to "strike down" and burn at the gas vent in the lower tube.

EXPERIMENT VI. An interesting experiment may be carried out in the following way: Close the lower end of a lamp chimney with a plaster plate or a thin paraffined cork, and cement a cap of wire gauze over the top. Bore two holes in the cork or plate, one three-eighths of an inch in diameter, the other to take a quarter-inch tube, B, which is connected with a gas tap. Turn on the gas at B until all air is swept out of the chimney, then ignite the escaping gas above the gauze, turn the supply down until the flame is steady, and hold a lighted match below the hole A.

What happens at A? What is burning at C? What is burning at A? Compare the luminosities of the flames? Why should there be a difference? Compare the conditions and the character of the flame at A with conditions and character of the blue cone in the flame of a Bunsen burner. Hold a strip of ignited touch paper so that the smoke will pass into A. State and explain the result observed.

This experiment might be repeated with certain other pairs of gaseous substances, as carbon monoxide and oxygen, chlorine and hydrogen, and oxygen and hydrogen.

The descriptions *combustible* and *supporter of combustion* must, therefore, be taken in a somewhat modified sense from that commonly used. In the case of two gases which by their combination produce light and heat, it is customary to say that the one which is projected into the other burns in it, while the one which surrounds the flame is named the supporter of combustion; but if the gases be mixed and ignited it can only be said that *they* burn, not that either burns in the other.

PROBLEMS

1. Examine the flame at a common fish-tail gasburner.

How may it be divided in regard to luminosity? Is there any combustion going on in the dark part near the jet? How may the flickering streaks of light in that dark zone be accounted for? State and explain the phenomena observed when the burner is gently tapped.

2. Cover the holes in the base of the burner of a coal oil lamp.

What alteration does this produce in the flame? Why does the flame change in its character? Why does such a lamp smoke if the flame is turned too high? What purpose does the chimney serve on a coal oil lamp?

3. Fire damp, the explosive gas found in coal mines, is Methane, CH_4 , a hydrocarbon that ignites at a comparatively low temperature, and burns to carbon dioxide and water.

Explain why fire damp is explosive when mixed with air. Why is a miner's naked light or tobacco pipe a source of danger in coal mines, but the safety lamp is not? Why should the miners name the gas *choke damp* that remains after an explosion of *fire damp*?

4. Of what does the dense black smoke consist that sometimes comes out of factory chimneys?

From the experiment with the candle flame, explain how that smoke may have been produced?

5. If a lamp be carried from a warm room into a very cold one there will be a distinct shrinkage of the flame in size. Why?

6. What is meant by the draught of a furnace or stove? Of what service is it? Forced draught is used in locomotive furnaces, and frequently in factory furnaces. What does the term mean and what is the purpose of that kind of draught?

CHAPTER XXXIX

ILLUMINANTS

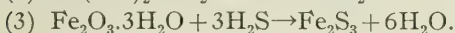
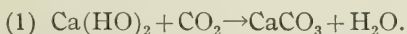
Petroleum.—The origin of the mineral oil known as Petroleum is not certainly known, but it is probable that some deposits of it are formed by the natural distillation of animal and vegetable matters contained in beds of shale in the earth's crust. An oil very similar to crude petroleum is obtained from such shales by artificial distillation. Petroleum is a thick, dark, tarry-looking liquid, which consists of a mixture of hydrocarbons of various kinds; but those of the oil of Pennsylvania, Ohio and Ontario are mainly of the paraffine series, having the general formula C_nH_{2n+2} , as CH_4 , C_2H_6 , C_3H_8 , $C_{28}H_{58}$. These hydrocarbons are of different volatilities, so the mixture may be readily separated by distillation into a number of parts, each suited for a particular use. This *refining*, as it is called, is usually done in two stages; the first yields the more volatile ingredients as gasoline, and kerosene; the other yields the thicker, heavier substances, as lubricating oils, vaseline, paraffine wax; there is also some coke formed during the process.

The crude petroleum, as it comes from the wells, is heated for about 60 hours in stills of about 1,000 barrels capacity; the light oils are distilled over first at a comparatively low temperature and the products below a specific gravity of .729 are kept separate. This fraction contains such substances as gasoline and benzine, which are further separated by a careful redistillation. The next fraction is removed when the specific gravity reaches

.79; this contains the various grades of coal oil. The more volatile kerosene has a flashing point of 110° F., the less volatile flashes at 150° . *Flashing point* is that temperature at which the liquid gives off enough vapour so that a momentary flash plays over its surface when a flame is brought near it. Oils of low flashing point are more dangerous to use than those that flash at a higher temperature. Sulphur impurities are removed from coal oil by the use of oxide of copper, which changes to a sulphide; and tarry substances are taken out by sulphuric acid. After the kerosene is separated from the material in the still the distillation of the residue is carried farther, and the distillates that come off are increasingly dark, heavy and thick. The first portions form the various lubricating oils, and run from thin mobile fluids to heavy semi-solid cylinder oil. If the redistillation of this fraction be carried on under reduced pressure, one substance obtained is the semi-solid "vaseline" or petrolatum of commerce. The coke that remains in the still after the distillation is completed is the material from which electric light carbons are made.

Coal Gas.—This is the volatile combustible matter which coal loses when strongly heated. To be valuable for gas-making, a coal should lose on heating from 35 to 60% of its weight. Such a coal is charged into white-hot fire clay retorts in lots of about 350 lbs. These retorts are the shape of half cylinders resting on their flat sides, and are about ten feet long, twenty inches wide and thirteen inches high inside. Their walls are about two inches thick. They are usually set in banks of six, heated by one furnace. Each retort projects beyond the front wall of the furnace and is closed by a cast iron mouthpiece. The gas from the retorts is led into an upright pipe, from which it passes into the hydraulic main, a long horizontal

pipe carrying some slowly flowing water, which dissolves part of the ammonia out of the gas and precipitates some of the tarry substances by cooling them. An exhaust pump draws the gas from the hydraulic main through the condenser, scrubbers and purifiers. The condenser consists of a bank of iron pipes like inverted U tubes, whose mouths dip into water in a trough; here most of the ammonia and tar are removed. The scrubber is a tank in which are revolving paddles that dip into water, and the gas is there agitated in contact with an extensive wet surface. Thus the last of the ammonia and some of the carbon dioxide and hydrogen sulphide are eliminated. The purifiers consist of tanks containing lime and hydrated oxide of iron spread on perforated shelves so as to expose a large surface to the action of the gas. The purpose of these materials is to remove carbon dioxide and hydrogen sulphide. The following equations express the reactions that go on here:

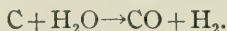


A ton of good gas coal yields 10,000 to 12,000 cubic feet of gas, 1,300 lbs. of coke, 13 gallons of tar, 5 lbs. of ammonia gas, and a varying quantity of other by-products.

Water Gas.—About two-thirds of the cities and towns of America use water gas for lighting and cooking purposes. This gas is essentially a mixture of hydrogen and carbon monoxide produced by the decomposition of steam by white-hot coal or coke. The reaction is quite similar to that by which hydrogen is set free when steam is passed over red-hot iron or magnesium (see experiment). In this case, however, the oxide formed is volatile and mixes with the hydrogen. As both gases are readily combustible in

air and set free a large quantity of heat the value of the mixture is at once apparent.

The chemical action is represented by the equation



A cylindrical generator (kiln) about 18 feet high and 10 feet in diameter is made of sheet steel and lined with fire brick. This is charged with broken coke or coal, which after being ignited is brought to a white-hot condition by passing an air blast through it. The temperature is thus brought to about 1100°C . This stage of the process is known as the *blow*, and the gas produced in the kiln at this time is a mixture of carbon monoxide and nitrogen, called *Producer Gas*; in this case it is led away and used for heating the carburetter. When the coal in the generator reaches the proper temperature, the air is shut off, and steam is passed in. The gas now formed is led to a tower filled with fire bricks, built in a checker-work pattern and heated to redness. This is the *carburetter*. At the entrance to this tower the gas that comes from the generator is mixed with a spray of crude petroleum. The oil is in part vapourised, in part decomposed to lighter materials that do not again combine, and the entire mixture is carried along to the gas holder, and forms the water gas of commerce. The oil is added because both carbon monoxide and hydrogen burn with non-luminous flames, hence some gas that will readily decompose and yield the requisite free carbon for light-giving purposes is required. The decomposition of the steam and of the oil both absorb much heat energy, so that this part of the process, called the *run*, can go on for only ten or fifteen minutes at a time. Then the steam is shut off and the air blast turned in again. Thus *blows* and *runs* alternate for about twelve to fifteen minutes each.

About 350 lbs. of coke will produce 10,000 cubic feet of water gas, which will be from 25% to 35% carbon monoxide. On account of the actively poisonous nature of the latter compound great care should be taken to prevent the leakage of any of the gas into air that is likely to be breathed.

The substance referred to as *producer gas* is coming to be extensively used as a fuel in industrial works. Formerly it was simply carbon monoxide mixed with nitrogen and a little carbon dioxide. It is found, however, that a gas of much greater heating power can be obtained by mixing steam with the air before the latter is forced into the white-hot carbon. This will result in the production of a mixture consisting of carbon monoxide, hydrogen and nitrogen. When the gas is to be burned for heat, a cheap grade of coal may be used, but if it is employed for gas engines, it must be free from tarry substances, and is then prepared from coke. In either case it is a cheap, serviceable and efficient source of power.

Gas Mantles.—From the experiments it is clear that a flame is rendered luminous by the presence in it of incandescent solids. The ingenious invention of Auer Von Welsbach enables us to take advantage of this fact to greatly improve the illumination of buildings. It is known that the incandescent oxides of some metals, as zinc, magnesium, calcium, cerium and thorium, glow very brightly, the two latter ones becoming especially brilliant at the temperature of a gas flame. To prepare the mantle a cylinder of knitted cotton is dipped into a solution of the mixed nitrates of cerium and thorium; this is afterwards dried and suspended over a gas flame; the cotton fibre is burned out, leaving a frail cylindrical skeleton of the oxides of the metals. When this is placed in the non-luminous flame of a Bunsen burner the mantle

glows so brilliantly that it yields about five times the light that would be obtained from the same quantity of gas burned in the ordinary way.

The Oxyhydrogen Flame.—When hydrogen burns in air a great amount of energy in the form of heat is set free. If oxygen be used instead of air the rate of reaction is hastened and a corresponding rise of temperature occurs. If still further, oxygen be projected into the mass of burning hydrogen the reaction becomes yet more rapid and the heat given off is greater. Before electricity became available for common use the oxyhydrogen flame was the means by which both one of the brightest forms of illumination

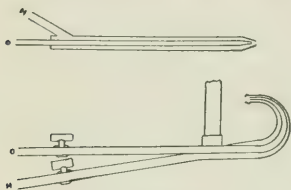


FIG. 11

and one of the highest artificial temperatures were obtained. The necessary combustion was secured by blowing a jet of oxygen into a mass of burning hydrogen. This required a special appliance known as the oxyhydrogen burner.

The upper figure shows the structure of such a blow-pipe, as used for heating; the lower one, of a lantern burner, as used for lighting. In the latter case the flame plays on a cylinder of lime (calcium oxide), which, when heated to incandescence, gives off a very brilliant white light. This was named the Lime Light, from the material employed in its production, and the Drummond Light from the inventor. The gas mantle of the previous paragraph is an application of the principle employed in the lime light, but the thin film of solid and its high luminosity at incandescence make the mantle both more economical and serviceable than lime cylinders as a source of light.

K_2CO_3 & H_2O washing soda

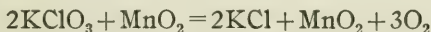
CHAPTER XL

QUANTITATIVE COMPOSITION OF COMPOUNDS

I

Carbon monoxide consists of 12 parts by weight of carbon and 16 of oxygen. It is therefore three-sevenths carbon and the rest oxygen. This is generally expressed as carbon 42.85% and oxygen 57.15%. Similarly the molecular weight of KNO_3 is 101, and of these 101 parts, by weight, potassium makes up 39, nitrogen 14, and oxygen 48; then, of the whole, 38.6% is potassium, 13.8% nitrogen, and the rest oxygen.

II



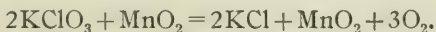
In this case the oxygen is derived from the potassium chlorate, and if the action goes on to completion, the quantity of oxygen obtained will be limited by the quantity of chlorate present. If 50 grams of the chlorate were heated, how much oxygen could be obtained from it?

Starting with the equation given above,

245 parts of chlorate yield 96 of oxygen,

$$50 \text{ yield } \frac{96 \times 50}{245} = 19.6 \text{ grams.}$$

How much chlorate must be taken that 16 grams of oxygen may be obtained from it?



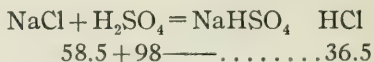
245 parts by weight of chlorate yield 96 of oxygen.

How to determine the percentage composition of a substance when the weight of each element taken are known.

Since 96 grams of oxygen come from 245 of chlorate,

$$16 \text{ would come from } \frac{245 \times 16}{96} = 41, \text{ nearly.}$$

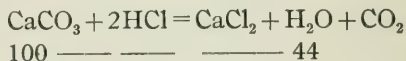
In a certain manufacturing operation there is used hydrochloric acid of that degree of concentration obtained by dissolving one part by weight of hydrogen chloride gas in four parts by weight of water. To prepare this gas what quantity, by weight of sodium chloride and of sulphuric acid, must be taken per litre of water used?



Each litre of water requires 250 grams of hydrogen chloride, and we learn from the equation that 36.5 grams of hydrogen chloride are obtained from 58.5 of sodium chloride and 98 of sulphuric acid; then 250 grams of hydrogen chloride come from $\frac{585}{365} \times 250$, and $\frac{980}{365} \times 250$ grams of sodium chloride and sulphuric acid respectively.

III

What volume of carbon dioxide measured at standard temperature and pressure will be obtained by treating 40 grams of calcium carbonate with an excess of hydrochloric acid?



100 grams of the carbonate yield 44 of the dioxide, hence 40 grams of the carbonate yield $\frac{44 \times 40}{100} = 17.6$ grams of carbon dioxide. This weight has to be transformed

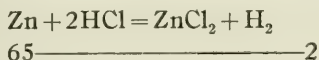
into volume, and the basis of such change is, in all cases, that one gram-molecule of the gas occupies 22.4 litres at standard. Then 44 grams of CO_2 occupy 22.4 litres,

therefore 17.6 grams occupy $\frac{22.4 \times 17.6}{44} = 8.96$ litres.

Putting this in one statement it becomes $\frac{44 \times 40}{100} \times \frac{1}{44} \times \frac{224}{10}$

(1) How much zinc must be taken so that when it is treated with excess of hydrochloric acid there will be just hydrogen enough to fill a 10 litre tank, the gas being at standard temperature and pressure?

(2) If the temperature were 27°C. and pressure $2\frac{1}{2}$ atmospheres, what weight of zinc would be required?



65 grams of zinc yield 2 grams of hydrogen; but 2 grams of hydrogen occupy 22.4 litres. Then 22.4 litres of hydrogen are produced by the action of 65 grams of zinc on acid. 10 litres would be produced by the action of

$$\frac{100}{224} \times 65 \text{ grams, or } 29 \text{ gr.}$$

(3) To solve the second part of the question it is necessary to find what volume the gas in the tank would occupy at standard temperature and pressure, then find the weight of this volume, then the weight of zinc necessary to set it free.

10 litres of gas at 0°C. , become $10 \times \frac{300}{273}$ litres at 27°C. , hence

$$10 \text{ litres at } 27^\circ \text{C.}, \text{ change to } 10 \times \frac{273}{300} \text{ litres at } 0^\circ \text{C.}$$

Next make the necessary reduction for pressure $10 \times \frac{273}{300}$

litres at a pressure of $2\frac{1}{2}$ atmospheres become

$$10 \times \frac{273}{300} \times \frac{2\frac{1}{2}}{1} \text{ litres} = 10 \times \frac{273}{300} \times \frac{5}{2} \text{ litres at standard.}$$

But $\frac{224}{10}$ litres weigh 2 grams,

$$\text{therefore } 10 \times \frac{273}{300} \times \frac{5}{2} \text{ litres weigh } 2 \times \frac{10}{224} \times 10 \times \frac{273}{300} \times \frac{5}{2} \\ \text{grams} = \frac{65}{32} \text{ grams.}$$

But 2 grams of hydrogen are set free by the action of 65 of zinc,

hence $\frac{65}{32}$ grams are set free by $\frac{65}{2} \times \frac{65}{32}$ grams of zinc or

66 grams, nearly.

PROBLEMS

1. How much oxygen, by weight, can be obtained from 245 grams of chlorate of potash, heated with manganese dioxide? What would be the volume of this oxygen at atmospheric pressure if passed into a tank surrounded by water and broken ice?

2. Calculate the percentage composition of carbon dioxide, and of carbon monoxide. Since there is a single carbon atom in each compound, why does the percentage of carbon vary? How much oxygen in the dioxide is combined with 27.27 parts by weight of carbon? How much oxygen in the monoxide is combined with the same weight, 27.27 parts, of carbon? What relation is there between these two quantities of oxygen? Refer to the Law of Multiple Proportions.

3. A certain compound of iron and sulphur, when analysed, yielded 63.63% iron and 36.36% sulphur. A chemist wishes to

make 10 grams of this compound by causing iron and sulphur to combine, how much of each should he weigh out?

4. What is the percentage composition of magnesium oxide?

5. How much nitrous oxide may be obtained from 80 grams of ammonium nitrate? What volume would this quantity of gas occupy at standard temperature and pressure? What volume would it occupy in a room in which a centigrade thermometer marks 18° , and the barometer stands at 758 mm.

6. What does a litre of each of the following gases weigh: Ammonia, carbon dioxide, hydrogen chloride, acetylene, nitrogen, sulphur dioxide?

7. 24.5 grams of potassium chlorate are mixed with 10 grams of manganese dioxide, and heated until no more gas passes off; what will be the weight of the part left in the tube? If this residue be warmed with sulphuric acid what further chemical action will occur and what weight of gas will be given off?

8. If 6.3 grams of copper dust were spread in a tube in a thin layer and 10 litres of air drawn slowly over it while it is heated to redness, what would be the gain in weight of the tube containing the copper? What would be the decrease in volume of the air?

9. If none of the products be lost, what weight of water gas will be formed for each gram-molecule of steam decomposed by the carbon? What will this water gas measure at standard?

10. If a flask whose capacity is 600 c.c. be filled with carbon monoxide gas and weighed, and if the weight be .7524 grams more than that of the flask exhausted of air, what is the molecular weight of carbon monoxide?

11. In a certain reaction 12 grams of oxygen were set free; what volume would it occupy, at standard? If the gas in this problem were measured at 30° C. and 700 mm. pressure, what two correction factors would have to be introduced?

12. If a mole of oxygen were driven into a tank under a pressure of 5 atmospheres, the tank being immersed in ice water, what would be the density of the gas? If the tank were then taken out and put in boiling water, what would be the density of the gas? Would the same pressure retain the gas at the same volume in the second case as in the first? What pressure would do so?

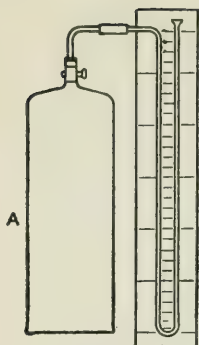


FIG. 12

13. The tank A has nitrous oxide, N_2O , forced into it until the gas is at such pressure that when connected with an open mercury manometer the mercury rises in the open arm to 114. When the manometer is disconnected the mercury stands at 76 in both arms and the divisions are centimetres. What is the weight of the gas in the tank in grams, if the capacity of the tank is 25 litres? If the mercury stood at 114 in the other arm (the left-hand one), what would be the interpretation of it; and what would be the weight of the gas in the tank then?

14. If the accompanying figure shows the dial of a pressure gauge and the graduations are in pounds, what would be the volume of gas at standard temperature and pressure if, when the gauge is attached to the tank mentioned in the previous problem, and the tap opened, the hand moved round to 28 and stood there?

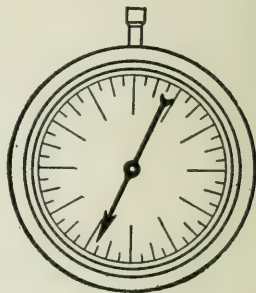


FIG. 13

CHAPTER XLI

CALCULATION OF FORMULÆ

To construct the formula of a compound we must know its percentage composition and the density of its vapour, or the density of the substance itself if it is a gas at ordinary temperatures. When the vapour density is not known, the simplest grouping of the atoms in the proportion in which they occur is taken as a formula for the substance.

(1) A compound of carbon and oxygen gives, on analysis, 42.85% carbon and 57.14% oxygen; its density is 14, what is its formula? We have learned that the unit combining mass of carbon is 12 times, and that of oxygen 16 times, as heavy as the corresponding hydrogen unit. If, then, we divide the carbon percentage by 12, and that of oxygen by 16, we shall get the relative numbers of unit combining masses, or atoms, in the molecule. These quotients are both 3.57, hence for every 3.57 atoms of carbon there are 3.57 atoms of oxygen, or the numbers of atoms of the two constituents are the same. This decides one point, viz., that the formula is CO, or C_2O_2 , or C_3O_3 , or generally C_xO_x . Now comes in the condition of density. We know from the density given that the molecular weight is 28, hence the formula must be CO.

(2) The analysis of a certain substance yielded calcium 40%, carbon 12%, oxygen 48%. Write the simplest formula for it?

Proceeding as before—

40	per	cent.	divided	by	40	gives	1
12	“	“	“	“	12	“	1
48	“	“	“	“	16	“	3

The numbers of atoms in the molecule are 1 of calcium, 1 of carbon, 3 of oxygen, hence the accepted formula is CaCO_3 , since the gas density of the substance is not given.

(3) A compound gave on analysis—sodium 32.32%, sulphur 22.53%, oxygen 45.06%; calculate the simplest formula for it.

If 32.32	be	divided	by	23	the	quotient	is	1.4
If 22.53	“	“	“	32	“	“	“	0.7
If 45.06	“	“	“	16	“	“	“	2.8

and the simplest proportion existing among these numbers is 2 : 1 : 4; hence for *once* the atomic weight of sulphur, there are *two* atomic weights of sodium and *four* of oxygen, then the formula will be Na_2SO_4 .

(4) 1.72 grams of a certain mineral was analysed with the following results: When heated it gave off .36 grams water, it contained 1 gram SO_4 and .4 grams calcium; what was its composition?

36	divided	by	18	gives	2	as	a	quotient.
100	“	“	96	“	1	“	“	“
40	“	“	40	“	1	“	“	“

These numbers are obtained by moving the decimal point two places to the right in the numbers expressing the quantities, so as to eliminate the fractions; then dividing each by the weight of the atom or group of atoms composing that substance whose percentage is being dealt with. The composition is one part of calcium, one part of sulphuric acid radical, and two parts of water.

The formula, therefore, is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. (For explanation of this formula see next chapter.)

PROBLEMS

1. A certain compound of oxygen and nitrogen is composed of nitrogen to the extent of 46.67%, the density of the compound is 15. What is its formula?

2. 2.46 grams magnesium sulphate yielded 1.26 grams water, .96 grams sulphuric acid radical, and .24 grams magnesium. What formula expresses its composition?

3. A compound of carbon and hydrogen that exists as a gas has a density of 14, $\text{H} = 1$. It is composed of carbon 85.71%, hydrogen 14.28%. What is the molecular formula?

4. A certain specimen of nitric acid has a specific gravity of 1.48; and for a reaction 50 grams of this acid are required, how many c.c.'s of it should be taken?

5. A compound of carbon and hydrogen has a vapour density of 38.9 approximately, and it is 92.3% carbon; write the formula for it. If the vapour density were given as 12.9, what would then be the formula?

6. 6.32 grams of copper oxide, when heated in a tube with a current of dry hydrogen passing over it, changed to 5.04 grams of copper dust, and the substance that passed out of the tube weighed 1.44 grams. Find the percentage composition of copper oxide; and knowing that the atomic weight of oxygen is 16 and the formula for copper oxide is CuO , find the atomic weight of copper.

7. $\text{CaO} + 3\text{C} \rightarrow \text{CaC}_2 + \text{CO}$. According to this equation, how much coke and lime will be required to make a ton of calcium carbide? If a certain weight of this carbide was treated with water and the following reaction occurred, $\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{HO})_2 + \text{C}_2\text{H}_2$, and if the calcium hydroxide when dried weighed 185 grams, find the volume of acetylene set free, at standard.

8. When pure copper oxide is heated in hydrogen, determine the weight of water that will be produced for every 10 grams of oxide reduced.

9. A compound of nitrogen and oxygen is composed of nitrogen 30.435%, oxygen 69.565%. At ordinary temperatures the density is 46, but as the temperature is raised this density grows gradually less, and when the gas is heated to 150° C. the density becomes constant at 23. What is the formula for the gas in the first case; what in the second? How is the change of density accounted for?

10. Sulphur vapour at about 450° has a molecular composition probably represented by S_8 ; at 1000° it is represented by S_2 . What are the corresponding changes in density and in volume, due to change of temperature and molecular structure, while pressure is constant?

CHAPTER XLII

WATER OF CRYSTALLISATION

When copper sulphate crystallises out of solution it forms rather handsome rhombic crystals of a bright blue colour. These, though perfectly dry, will give off water when heated; and they then become changed to a bluish grey powder. If water is added to this powder the blue colour is restored, and whatever of the powder is dissolved will recrystallise as before when the water evaporates. The experiments with sodium carbonate, ferrous sulphate and magnesium sulphate illustrate the same phenomena in these substances.

It seems then that each molecule of such salts on crystallising out of solution enters into combination with a definite quantity of hydrogen and oxygen. These compounds are known as hydrated forms of the salts. It is evident that the crystalline structure in these cases is dependent on the presence of the elements of water, because if the latter be removed the crystal will be destroyed. The union between the molecules of the salt, CuSO_4 , and the hydrogen and oxygen, is generally quite weak, so that a moderate heat causes a dissociation, but the gases form water in the process. Further, in most cases some portions of the hydrogen and oxygen are held less firmly in the union than others. For instance, the common hydrated form of copper sulphate is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; this when heated dissociates, thus $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 3\text{H}_2\text{O} + 2\text{H}_2\text{O}$; and the trihydrated sulphate on further heating loses more water, finally becoming anhydrous

(waterless) sulphate of copper, represented by CuSO_4 . Some hydrated salts lose water of crystallisation on exposure to air, thus sodium carbonate, a hard, crystalline, ice-like solid, having the composition $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, when exposed in an open vessel falls to a fine white powder represented by $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.

The chemical properties of the anhydrous salts and of their hydrates are the same, so that they react in the same way. The following are some formulæ of common hydrated compounds: (1) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; (2) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; (3) $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$; (4) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; (5) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; (6) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; (7) $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The names of the preceding salts taken in order are: (1) copper sulphate (blue stone); (2 and 3) sodium carbonate (washing soda); (4) sodium sulphate (Glauber's salt); (5) magnesium sulphate (Epsom salt); (6) iron sulphate (copperas); (7) potassium aluminium sulphate (alum).

This loss of hydrogen and oxygen by hydrated salts may be compared to the dehydration of carbohydrates by sulphuric acid. Thus $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ becomes $12\text{C} + 11\text{H}_2\text{O}$, starch, $\text{C}_6\text{H}_{10}\text{O}_5$, and cellulose, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, undergo similar decompositions. (See page 121).

Substances that lose water of crystallisation in the air and fall to powder are said to effloresce, while those that absorb water and become pasty or liquid are said to deliquesce. The substances are then efflorescent or deliquescent.

PROBLEMS

1. If 28.6 grams of soda crystals, hydrated sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, were treated with excess of hydrochloric acid, what weight of carbon dioxide would be obtained?

2. A manufacturer who uses carbon dioxide in his business can buy hydrated sodium carbonate at \$20.00 a ton; what could he afford to pay for the carbonate as white powder, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$?

3. Given that the formula for ferrous sulphate, green vitriol or copperas, is $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, how many lbs. of water does a man buy who purchases 100 lbs. of the hydrated salt?

4. A certain prescription called for 477 grams of anhydrous copper sulphate. This substance was not available, but the hydrated sulphate, known as blue stone, or blue vitriol, was obtainable. How much of the latter should be taken if its composition is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$?

5. If a manufacturer buys bleaching powder at \$40.00 a ton to extract the chlorine from it, what could he afford to pay per 100 lbs. for liquid chlorine, neglecting the expense of getting the chlorine from the bleaching powder?

CHAPTER XLIII

CATALYSIS

In the preparation of oxygen from potassium chlorate, it was found that the presence of manganese dioxide materially hastened the rate of the reaction, though there was no alteration either in the composition or quantity of the dioxide. Again, when sulphur dioxide and oxygen are heated together there is no perceptible amount of union between them in any reasonable period of time; but if platinum be present the reaction proceeds at a measurable rate, and the greater the metallic surface exposed to the gases the more rapidly they combine.

These are examples of the phenomenon known as **Catalysis**. In one case manganese dioxide is the catalyser or catalytic agent; in the other, platinum. Catalysis may be defined as a modification of the rate of reaction between two substances, due to the presence of a third body which does not itself undergo any permanent chemical change, and which is not a diluent of one or both reacting substances.

This statement requires a word of explanation on each of two points, viz., rate of reaction and permanent chemical change. It is customary to say that oxygen and hydrogen do not combine at ordinary temperatures; the chemist prefers to consider the reaction as going on, but at an exceedingly slow rate. It is known, for instance, that an explosive mixture of oxygen and hydrogen, if sealed in a tube and allowed to stand in a room in which the temperature is 60° or 70° F., will show a contraction of volume after several months, and the reduction is at-

tributed to a union of portions of the gases. It is on this account that catalysis is spoken of as a change in the rate of reaction, rather than a cause of the reaction.

In regard to the other point of *permanent* chemical change, it may be possible that there is a reaction between the catalyser and one of the reacting substances, in some cases. For instance, an attempt has been made to explain the effect of manganese dioxide on potassium chlorate by assuming that the heptoxide of manganese, Mn_2O_7 , is formed by deoxidation of the chlorate, and that this oxide undergoes decomposition, setting free the oxygen. This is only a conjecture, but there are two chemical facts that give it some slight appearance of reality: (1) There is a heptoxide of manganese known, (2) In many chemical decompositions the presence of a substance with which one of the constituents may combine aids the reaction. For instance, common quartz is composed of two elements, silicon and oxygen; the former combines readily with chlorine, when free, and the latter with carbon. If quartz be powdered and heated it does not undergo decomposition, neither does it change when heated with chlorine, nor with carbon. But if it be heated in presence of both chlorine and carbon, it forms chloride of silicon and oxide of carbon, thus showing the influence of combined chemical attraction in producing an alteration of composition.

It is more reasonable to view catalytic action as due to chemical attraction among the substances present than as a mysterious result of some unknown force.

If such temporary changes occur, the reactions by which they are produced are reversible, and the final form of the catalyser is the same as the first one.

Water is probably the most common catalyser known, but it is of such general occurrence, especially as vapour,

that it is only lately its importance in this respect has been recognised. Platinum causes several reactions to go on somewhat rapidly, that otherwise would be too slow for recognition. The self-lighting gas jets are an application of this principle to common use, for a bit of platinum sponge (finely divided metallic platinum) causes the escaping gas to combine with the oxygen of the air with sufficient vigour to produce heat enough to start ignition.

*Water is the fastest known catalyst
known to P.M. & Co*

CHAPTER XLIV

SULPHURIC ACID,

It has already been found (page 39) that sulphur, by proper treatment, may be made to yield two oxides, SO_2 and SO_3 . Each is the anhydride of an acid, so that when dissolved in water they form sulphurous and sulphuric acids respectively. The latter, on account of its industrial importance, calls for some consideration.

The manufacture of sulphuric acid depends upon the oxidation of SO_2 to SO_3 , but this cannot be done by direct union of the dioxide and oxygen. The process of oxidation is a catalytic one, and in practice is accomplished by the use of either of two agents, powdered platinum, or nitrogen peroxide; these methods are respectively known as the contact process and the chamber process. In the former the gases sulphur dioxide and oxygen, or air, are led over sheets coated with platinum powder and heated to redness. The gases combine and the compound, SO_3 , is dissolved in water.

In the chamber process sulphur dioxide is mixed with air, nitrogen peroxide, and steam, in large leaden chambers, in which a chemical reaction occurs that ends in the production of sulphuric acid, nitrogen and nitrogen peroxide. A theory has long been held that the nitrogen peroxide yields up part of its oxygen to the sulphur dioxide, thus $\text{NO}_2 + \text{SO}_2 \rightarrow \text{SO}_3 + \text{NO}$, and that the nitric oxide takes up oxygen from the air, as it certainly will do (Experiment 69). The weak points of the theory are that it has not been demonstrated that nitric oxide is

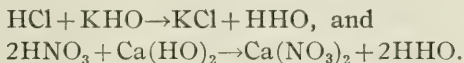
formed in the process, and there is good reason for believing that the reduction of nitrogen peroxide to the dioxide is very seldom a single step, but that the result is a mixture of oxides. The statement may be left, then, that the action is catalytic because the nitrogen peroxide is found at the end of the operation, as well as at the beginning.

Sulphuric acid is a syrupy liquid having a specific gravity of 1.8; it boils at 330° , and on account of its high boiling point it is very useful for displacing other acids from their compounds. One of its characteristic properties is its energy in uniting with water to form a hydrated acid. On this account it is used for drying gases and for abstracting the elements of water from many organic compounds (Experiments 16, 101). Sulphuric acid, like nitric, acts as an oxidising agent with nascent hydrogen, thus $\text{H}_2\text{SO}_4 + 2\text{H} \rightarrow 2\text{H}_2\text{O} + \text{SO}_2$. This is the basis for the method of preparing sulphur dioxide from sulphuric acid and copper. Sulphates are common among minerals, as gypsum, epsom salts and heavy spar. The test for the presence of sulphuric acid, or of any soluble sulphate, consists of a solution of a barium salt, as the chloride or nitrate. Barium sulphate is an insoluble salt, hence is thrown down as a white precipitate, when barium ions are present in a solution containing sulphuric acid ions.

CHAPTER XLV

BASICITY OF ACIDS

If an acid whose composition is represented by the formula HNO_3 or HCl reacts with a base of the type KHO or $\text{Ca}(\text{HO})_2$, there will commonly be but one salt formed, and in it the entire hydrogen of the acid molecule or molecules reacting will be replaced by the metal of the base, thus:



We have, however, met the formulæ KHSO_4 and $\text{CaH}_2(\text{CO}_3)_2$, as expressing the composition of salts, and it is now time to enquire how such compounds are produced.

H_2CO_3 and H_2SO_4 are, respectively, the formulæ for carbonic and sulphuric acids. Such salts of these acids as NaHCO_3 , KHSO_4 , indicate that the ionisation of the acid in solution takes place in stages, thus: (1) H_2SO_4 becomes $\overset{+}{\text{H}}, \overset{-}{\text{HSO}_4}$ which further becomes $\overset{+}{\text{H}}, \overset{+}{\text{H}}, \overset{-}{\text{SO}_4}$. If, then, a limited quantity of the base is present the combination among the ions apparently takes place when only one hydrogen ion has split off, thus, $\text{H}_2\text{CO}_3 + \text{KHO} \rightarrow \overset{+}{\text{H}}, \overset{-}{\text{HCO}_3} + \overset{+}{\text{K}}, \overset{-}{\text{HO}} \rightarrow \text{KHCO}_3 + \text{HHO}$. The HCO_3 ion will undergo further dissociation into $\overset{+}{\text{H}}, \overset{-}{\text{CO}_3}$, especially if there are positive ions (cations) present, with which the $\overset{-}{\text{CO}_3}$ may form compounds that are more stable than the H_2CO_3 is. We then find that an acid which has two

hydrogen atoms in a molecule, may form two kinds of salts, depending on whether that salt is produced by an anion free from hydrogen or one that still has in it one atom of hydrogen. According to this, sulphuric acid may form salts of the type KHSO_4 or K_2SO_4 , and carbonic acid may yield carbonates of such composition as NaHCO_3 and Na_2CO_3 . The salts that have only half of their hydrogen replaced are still capable of setting free hydrogen ions in solution; they are known as *acid salts*, because they have the distinguishing property of an acid and the composition of a salt.

NaHCO_3 is a carbonate, hence a carbonate of sodium and hydrogen. It is named acid carbonate of sodium, sodium hydrogen carbonate or bicarbonate of sodium. Those salts, which are formed by the replacement of all the hydrogen in the acid molecule by a metal, are normal salts. Such terms as bicarbonate and bisulphate are descriptive of the composition of the salt in one particular, viz., that it has double the proportion of the acid radical in the molecule that the normal salt has, when the quantity of the metal is constant.

An acid which, in solution, sets free only one hydrogen ion from each molecule is a *monobasic acid*; nitric, hydrochloric and acetic acids are examples. If two hydrogen ions may be set free from the molecule, the acid is *dibasic*; sulphuric, carbonic and oxalic acids are of this class. A few acids are *tribasic*; phosphoric acid, H_3PO_4 , is a type of these.

The formation of acid salts generally takes place when there is a limited amount of the base present, that is, when there is excess of the acid. This is an example coming under a more general principle, that if the substances may form more than one compound under similar treatment, and if one of the substances be limited in quantity,

The number of an acid refers to the no. of atoms of H in the acid that is replaced by a metal.

that compound will be formed which permits this constituent to enter into the largest number of molecules. Carbon will combine with oxygen by heating to form either CO or CO₂, the former if the carbon is in excess. The same quantity of oxygen would produce fewer molecules of the dioxide.

PROBLEMS

1. Given that acetic acid has the formula HC₂H₃O₂; oxalic acid, H₂C₂O₄; tartaric acid, H₂C₄H₄O₆; and that only the hydrogen atoms represented at the beginning of each formula separate as ions in solution, write the names of the salts of which the following are the formulæ: KHCO₃, Na₂CO₃, CaH₂(CO₃)₂, Ca(NO₃)₂, NaC₂H₃O₂, Pb(C₂H₃O₂)₂, NH₄HC₂O₄, (NH₄)₂C₂O₄, KHC₄H₄O₆, Na₂C₄H₄O₆, NH₄HSO₄.

2. Write formulæ for sodium chloride, sodium carbonate, potassium hydrogen sulphate, bisulphate of sodium, acid carbonate of ammonium, zinc acetate and magnesium oxalate.

3. Phosphoric acid is represented by the formula H₃PO₄; this acid forms three salts with sodium called dihydrogen sodium phosphate, hydrogen disodium phosphate, and normal sodium phosphate. Write their formulæ.

What part is common to all three formulæ? Write symbols showing the stages of ionisation of phosphoric acid in presence of a base.

Making of Sodium

CHAPTER XLVI

ALKALINE METALS

Sodium

Sodium is a metal having the colour of silver and the hardness of wax; it floats upon water, and melts at 96° C. (Compare page 44.)

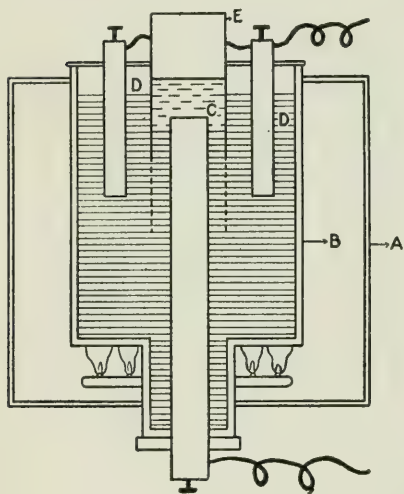


FIG. 14

In 1807 Sir Humphrey Davy prepared sodium by electrolysing sodium hydroxide; but that method of obtaining the metal was too expensive, until the recent electrical development has put a powerful and convenient agent at the chemist's disposal. At the present time sodium is prepared for commercial needs by electrolysing the hydroxide of the metal, where there is

an abundant supply of electrical energy available, at Niagara Falls, for instance. The method of preparation is known as the Castner process, and in outline is as follows: B is an iron tank set in a furnace, A, and filled with solid sodium hydroxide. There is a neck on the lower side of this tank which projects below the furnace, and

through it passes a thick iron bar, the cathode. An open iron cylinder is set in the top of the tank and projects downward into the sodium hydroxide; this is the anode; E is an iron cylinder surrounding the cathode, closed by a movable top, and having a cylinder of wire gauze attached to its lower end. The heat of the furnace fuses the hydroxide, except that in the neck; the sodium and hydrogen, as set free, collect at C and rise into E; the oxygen is liberated at D. The molten metal is dipped out of E at intervals.

Sodium Chloride occurs naturally in sea water, in many salt lakes, in some springs, and as beds of solid salt. Such beds exist, among other places, in the counties bordering southern Lake Huron, in northern New York, in England, and in Austria.

All the manufactured salts of sodium are prepared from the chloride, and so are the chlorine and hydrochloric acid of commerce; it is thus a very important substance in the world's industry.

Sodium Hydroxide was formerly prepared altogether by the action of slaked lime on sodium carbonate, thus $\text{Ca}(\text{HO})_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaHO}$.

The calcium carbonate was precipitated as a white salt, and the liquid evaporated to dryness. Sodium hydroxide is now prepared, to some extent, by electrolytic decomposition of brine, or of molten sodium chloride. In the Acker process, used at Niagara Falls, the molten salt is in a tank, at the bottom of which there is a layer of molten lead that forms the cathode. This absorbs the sodium as it is set free, and the metals are afterwards subjected to the action of steam that alters the sodium into the hydroxide and separates it from the lead. The chlorine liberated in this process is a valuable by-product for the manufacture of bleaching powder.

The diagram illustrates Castner's apparatus for the preparation of sodium hydroxide.

The tank is supported on an eccentric roller and a triangular bar. As the roller revolves the bottom of the tank is alternately raised and lowered at each end beyond the horizontal. The tank is in three divisions, but the partitions do not fit tightly against the bottoms of the recesses into which they dip. A layer of mercury, M, is

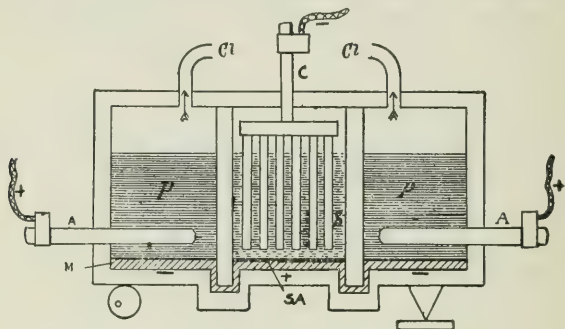


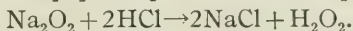
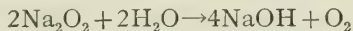
FIG. 15

poured in on the bottom; the two outside cells, P, are filled with strong brine and the middle one with water; A and C are the anodes and cathodes respectively. In the cells P the brine is decomposed, the sodium dissolving in the mercury, which here is the cathode, and the chlorine passing out at the top. The rocking of the tank causes the sodium solution in the mercury (amalgam) to rise to the highest part, therefore it flows into the middle cell, S. Here the mercury becomes the anode, and the sodium ions, passing to the cathode bars, are there changed by the water into the hydroxide.

Sodium hydroxide is a very deliquescent white solid. It corrodes or destroys animal tissues by uniting with some of their constituents. It forms compounds called *soaps* with the acids contained in both vegetable and

animal fats. These soaps are therefore sodium salts of the acids of fats. Potassium acts in a similar way, but the sodium salts solidify to form hard soaps, while those of potassium do not, and are known as soft soaps. This is the most important use of the hydroxide; but it is also largely employed to remove resins and gums from wood in the preparation of *chemical pulp* for paper making. Solid sodium hydroxide in a somewhat crude state is sold for household purposes as *concentrated lye*.

Sodium Peroxide.—If slices of metallic sodium be heated to redness in a tube in a current of air or oxygen, sodium peroxide, Na_2O_2 , will be formed. With water this produces sodium hydroxide and oxygen, and it is used as an oxidising agent in alkaline solutions. With acids it yields hydrogen peroxide.



Sodium Carbonates.—The normal carbonate of sodium, Na_2CO_3 , is commonly called washing soda; and the acid carbonate, NaHCO_3 , is the bicarbonate, or baking soda. The normal carbonate has an alkaline reaction, and crystallises from cold solution with 10 molecules of water per molecule of salt. It is used in scouring fabrics, in soap making, in the manufacture of glass, and as a source of carbon dioxide for commercial purposes. The bicarbonate is used mainly as an ingredient in baking powders, and as a source of carbon dioxide. In the process of baking it is necessary to make the bread light, that is, to prevent it becoming a solid mass. For this purpose baking powder, usually a mixture of bicarbonate of sodium and tartaric acid, is mixed with the paste of flour and water, and the heat and moisture cause carbon dioxide to be given off. The liberated gas puffs out the bread, as yet unhardened by baking.

Sodium Nitrate occurs in immense quantities as a mineral deposit in northern Chili and southern Peru. It is mined and shipped to Europe for use as a fertiliser and in alkali manufacture.

Sodium is one of a group, or family, of elements, known as the alkaline metals, the members of which resemble one another in characteristic properties, and in consequence form similar compounds. They all decompose water readily to form strongly alkaline hydroxides having the composition MHO , where M represents the element. Their corresponding salts tend to crystallise in the same way—the chlorides, for instance, in cubes—they all have a monad valency, and their properties generally alter in intensity either directly, as their atomic weights increase, or in the reverse of that order. The following table illustrates three of these particulars:

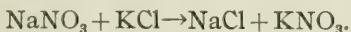
Name	Symbol	At. Wt.	Melting Point	Oxidation in Air	Action with Water
Lithium....	Li	7	180°	Slow	Slow
Sodium.....	Na	23	96°	Quick	Quick, but does not ignite
Potassium..	K	39	62.5	Rapid	Ignites
Rubidium..	Rb	85	38.5	Ignites on account of rapidity	Very vigorous with ignition

On account of their strong basic properties (setting free HO ions in solution), they combine very readily with acids to form a great number of salts, of such types as the following: MCl , MNO_3 , $MHCO_3$, M_2CO_3 , $MHSO_4$, M_2SO_4 , and $MC_2H_3O_2$.

Among the elements there are several groups that show relationships somewhat similar to those of the sodium family, and in the study of chemistry it is advantageous to consider the correspondences within the groups rather than to treat every element as a separate item.

Potassium

Potassium is the only other element of the sodium group that calls for consideration, because it alone approaches sodium in importance. The source of the potassium of commerce is mainly the Stassfurt beds of alkaline minerals in Central Prussia; here potassium chloride is found abundantly, combined with magnesium chloride as the mineral carnallite. Potassium nitrate is used largely in the manufacture of gunpowder, because it is an energetic oxidising agent, and when mixed with finely divided sulphur and charcoal, it causes a very rapid combustion. Potassium nitrate, popularly known as nitre or saltpetre, is mostly prepared from the Chili saltpetre (sodium nitrate) exported from South America. The chloride of potash from the Stassfurt beds reacts with the sodium nitrate to produce potassium nitrate and sodium chloride, thus:



Potassium Carbonate was formerly prepared by allowing water to filter through wood ashes; the soluble alkaline salts—mostly potassium carbonate—in the ashes were thus dissolved, the solution (lye) was afterward evaporated to dryness, and the solid residue calcined in iron pots. The product was named *pot ashes*. The present name of the metal is a latinised form of the old term for the salt. This carbonate is more deliquescent than that of sodium, and is used mostly in making chemical glassware.

CHAPTER XLVII

METALS OF THE ALKALINE EARTHS

Calcium, Strontium, Barium

These elements, though alkaline, are less markedly so than those of the previous group, so they form one link of connection between the light, active, alkaline metals and the heavy, somewhat inert metals of common use. The elements of this group can be set free from their compounds only with great difficulty; and, as they are not at present used to any extent, they are themselves little more than chemical curiosities. Many of their compounds, however, are plentiful and extremely useful. Calcium may be taken as the type of the family because its compounds are most abundant and most serviceable.

The metal is obtained by electrolysis of the fused chloride; it is white in colour and decomposes water to produce the hydroxide.

Calcium Carbonate exists as limestone, chalk, most kinds of animal shells, and marl; and when crystallised, it is marble, calcite, or crystalline limestone. All these are put to important uses. From this substance in its various forms we make roads, bridges, buildings, statuary, household ornaments, ornamental stone work, basins, mantels, lime and cement. When calcium carbonate is strongly heated it undergoes decomposition into carbon dioxide and calcium oxide or lime, CaO . The chemical reaction is a reversible one, and this has a very important industrial bearing. For instance, if lime be exposed to the air for a considerable time it will combine with the

carbon dioxide of the atmosphere to produce hard calcium carbonate again. When lime is made into mortar by mixing sand and water with it, the water dissolves carbon dioxide from the air, and the lime being strongly basic, the mortar turns into a mixture of calcium carbonate and sand. The *setting* of mortar is therefore a *chemical* process rather than a mere drying of the mass; the changing into the carbonate may continue for years, while the drying is done in a few days. The purpose of sand in mortar is mainly to form a layer of sufficient thickness to bind the units of the wall together, otherwise the mortar might be squeezed out from between the stones or bricks until it became so thin that it would not hold the parts in place. The sand is also believed to produce a more porous mass and thus permit the carbon dioxide to have freer access to the interior of the mass.

Chalk is calcium carbonate in the form of minute animal shells massed together; and marl, so common in the lakes of Ontario, has frequently, if not always, had the same origin. The shells of the oyster, clam, scallop and most of the larger animals that secrete such coverings, are pure calcium carbonate. Coral is also of the same composition, and is the skeleton of an animal which extracts the carbonate from sea water and builds it into reefs and islands.

Lime, CaO , when brought into contact with water, combines readily with it and evolves much heat in the reaction, $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{HO})_2$. The *hydroxide* thus produced is commonly called *slaked lime*, but the water may be again driven off by heating. Lime that has been exposed to the air for some time becomes air slaked, that is, absorbs moisture enough to become changed to the hydroxide; but at the same time, part of it changes back to the carbonate, as may be shown by testing it. Slaked

lime is slightly soluble in water, yielding an alkaline liquid called *limewater*, that is used as a test for the presence of carbon dioxide. When more lime is put into water than will be dissolved, and the solid particles in suspension form a more or less pasty mass, the mixture is known as *milk of lime* or *cream of lime*, depending on the consistence. The oxides of strontium and barium are formed in a similar way to that of calcium; they also form hydroxides with water, and these produce the carbonates on exposure to the action of carbon dioxide in solution, that is, to carbonic acid.

Calcium Sulphate, occurs in two forms, *gypsum* and *selenite*. The former is usually massive, soft and white; the latter crystallises in thin plates resembling mica, usually transparent, and so soft that they may be scratched by the finger nail. *Satin spar* consists of fine fibres of calcium sulphate arranged very closely together. All these contain water of crystallisation. When gypsum is heated to 200°C . it loses part of this water and becomes a fine white powder, called *Plaster of Paris*, because it was long ago made from material derived from beds beneath the City of Paris. This plaster has the power of again combining with water and *setting*, that is, becoming rigid, probably by resuming a crystalline structure. As plaster of paris expands when setting it will accurately fill a mould, hence is valuable for making casts, as it reproduces all details of form.

Calcium Phosphate occurs in Canada as bluish green or reddish brown crystals, consisting of hexagonal prisms capped by hexagonal pyramids (hexagonal means six-angled). Often, however, the crystals are not distinct, and the rock, still of the characteristic colours, forms the massive vein matter, or part of it, that fills fissures in granite or limestone. Formerly this mineral, known as *apatite*,

was largely mined in Ontario, and by treatment with sulphuric acid was changed into a mixture of calcium sulphate and a soluble phosphate which was extensively used as a land fertiliser under the name *superphosphate of lime*. Now a phosphate rock found in Florida and Georgia has supplanted the Canadian mineral because it can be put on the market at a lower price. The bones of animals, when calcined, so as to leave only mineral matters, consist of pure calcium phosphate, and when roasted and ground form *bone ash*, also a valuable fertiliser on account of the phosphorus in it.

Calcium Chloride, formed by acting on the carbonate with hydrochloric acid, is a useful drying agent in the laboratory after it has been calcined. It then acquires the power of absorbing water readily, and gases passed through it become free from moisture.

Cement is a compound of lime and burned clay. These have together the ingredients that, when calcined, produce a substance which becomes pasty with water, but soon sets, or changes to a rigid condition. Mixed with sand or broken stone it forms very hard and durable masses; and as it is easily moulded or run into convenient shapes, it is applicable to a wide range of uses. Portland Cement is prepared by making an intimate mixture of powdered limestone or marl with clay, about three parts of the first to one of the second; this is heated almost to fusion, cooled and ground to a very fine powder. Chemically, cement is a mixture of silicates of calcium and aluminium.

Glass is fundamentally a silicate of sodium or potassium and calcium or lead. Usually the carbonate of one of the alkaline metals is fused with ground quartz (white sand) and the other ingredients required to make the material suitable for the use to which it is to be put. Quartz is silicon dioxide, SiO_2 ; the anhydride of silicic acid, H_2SiO_3 .

hence glass is a salt of this acid. When quartz is fused with an alkaline salt a glass is generally produced, and often the rocks of which old lime kilns were built are glass-coated from the lime fusing with the silica in the wall rock, or in the mortar.

The strontium and barium compounds are not of so much importance, because they are not in such general use. Strontium occurs mainly as celestite (strontium sulphate) and strontianite (the carbonate). These are the compounds similar to gypsum and limestone. Strontium oxide, SrO , may be obtained from the carbonate by heating, but the temperature of decomposition is much higher than that required for limestone. The salts of strontium, mainly the chloride SrCl_2 and nitrate $\text{Sr}(\text{NO}_3)_2$, are used for producing the red fire in fire-works, because the vapours of these salts tinge flames crimson. Strontium hydroxide will form a chemical compound with sugar, and as this compound is only slightly soluble, the hydroxide is used to separate the sugar from the mixture of soluble impurities during the manufacturing process. After most of the sugar has crystallised out, strontium hydroxide is mixed with the remaining impure syrup, the liquid filtered off and the solid treated with carbon dioxide. The strontium carbonate that is finally formed is insoluble, hence the sugar may be obtained in pure solution.

The ores of barium are the carbonate and sulphate, the former named witherite and the latter barite or heavy spar. The compounds of barium that are chemically of most interest are the hydroxide $\text{Ba}(\text{OH})_2$, and the peroxide or dioxide, BaO_2 . The former is a valuable test for carbon dioxide and soluble carbonates, because it forms barium carbonate, an insoluble compound.

The dioxide is of value as a source of oxygen gas, as it readily becomes reduced to the monoxide, BaO . Brin's

process for obtaining oxygen from air makes use of this agent, BaO, to fix the oxygen by forming BaO₂; afterwards the reduction is carried out.

Barium sulphate is used as a pigment by painters, and it is a common adulterant of white lead. It has the merit, as a paint, of not turning brown when exposed to hydrogen sulphide in the air, as lead paint does.

This group furnishes another example of elements related in their properties; and varying in those properties either as the atomic weights of the elements change, or in the reverse way.

	Sym- bol	At. Wt.	Sp. Gr.	Chlorides	Hydrox- ides	Carbonates	Sulphates
Calcium...	Ca	40	1.65	Very soluble (deliques- cent).	Slightly soluble.	Practically insoluble.	Slightly soluble.
Strontium.	Sr	87.5	2.5	Less soluble.	More soluble.	Very slightly soluble.	Hardly at all soluble.
Barium....	Ba	137.5	3.8	Still less soluble.	Still more soluble.	Slightly more soluble.	Practically insoluble.

Hard Waters.—It has already been mentioned that soap is a soluble salt of one of the alkaline metals, potassium or sodium, with an acid of an oil or fat. If there be added to a solution of soap a solution of a salt of one of the heavy metals, as calcium, iron or lead, the alkaline metal will be displaced by the other one, and the new compound will not be soluble, but will form a curdy solid floating in the water. Such waters are described as *hard*, and the hardness is very often due to soluble salts of calcium, magnesium or iron, especially the carbonates contained in the water. The acid carbonate of calcium, CaH₂(CO₃)₂, is quite commonly contained in earth waters.

Normal calcium carbonate is but slightly soluble in water, as is shown by a deposit of this salt forming on the inside of vessels in which water from springs, lakes or streams has been boiled for a long time, such as tea-kettles and steam boilers. Pure water will dissolve only about 2 grains of calcium carbonate per gallon, but rain water that has dissolved carbon dioxide from the air will hold in solution about 50 grains of the carbonate per gallon. This is probably due to the formation of the soluble acid carbonate, thus:



This compound is decomposed at the temperature of boiling water into the original substances and the normal carbonate is precipitated on the bottom sheets of the vessel, as the very troublesome *fur* or *boiler scale*, which, because of its non-conduction of heat, causes steam users to go to a great deal of trouble and expense to both get rid of it and to prevent its deposition.

When the salt held in solution is precipitated the water becomes *soft*. This softening process may sometimes be brought about by boiling, and sometimes by adding lime or washing soda, $\text{CaH}_2(\text{CO}_3)_2 + \text{CaO} \rightarrow 2\text{CaCO}_3 + \text{H}_2\text{O}$.

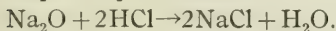
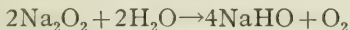
CHAPTER XLVIII

PEROXIDES

When sodium is heated in a tube in a current of air or of oxygen, it forms the dioxide or *peroxide*, Na_2O_2 . In this compound the oxidation is advanced a stage beyond the normal Na_2O . Barium dioxide is formed by concentration of oxygen in presence of heated barium oxide, BaO . If either of these peroxides be treated with cold dilute acid, hydrogen peroxide, H_2O_2 , will be obtained in solution.

Lead oxide in the presence of a strong oxidising agent, as nitric acid or chlorine, changes to the dioxide, PbO_2 , but this ranks with carbon dioxide and is not a peroxide in the same sense as the three compounds previously mentioned, because both lead and carbon have a well-defined valency of four, hence these dioxides are normal, though that of lead resembles the true peroxides in at least two important particulars, yielding oxygen when heated, and setting free chlorine from hydrochloric acid.

The peroxides readily yield oxygen; and with acids they yield both oxygen and the normal salts as final products.



The peroxides of sodium and barium when treated with cold dilute acid form hydrogen dioxide in solution; but

the latter substance is unstable and can be concentrated only with difficulty. The druggist's hydrogen peroxide is about a three per cent. solution. The peroxides are valuable as oxidising agents mainly because part of the oxygen is held very loosely in combination, and on decomposition of the compound the oxygen tends to unite with any substance present with which it can form a compound.

Closely related to the peroxides, if not indeed strictly classed with them, is ozone, one of the forms in which oxygen exists (an allotropic form of oxygen). It is formed commonly when an electric discharge passes between plates, and it gives the peculiar odour to the air surrounding an electric machine in action. Ozone is represented by the symbol O_3 , perhaps better by O_2O . Its preparation from oxygen and its decomposition are represented by $3O_2 \rightarrow 2O_3$; and in chemical reactions one atom of oxygen splits off from the molecule just as in the peroxides. Like them, it is very active chemically.

CHAPTER XLIX

LIST OF THE ELEMENTS

The following is a complete list of elements and their atomic weights, as now known. Column 1 contains the name of the element; 2, its symbol; 3, its weight referred to oxygen as 16; 4, an approximate weight that serves in ordinary calculations.

1	2	3	4
Aluminium . . .	Al	27.1	27
Antimony (Stibium) . .	Sb	120.2	120
Argon	A	39.9	40
Arsenic	As	75	75
Barium	Ba	137.4	137
Bismuth	Bi	208	208
Boron	B	11	11
Cadmium	Cd	112.4	112
Cæsium	Cs	132.9	133
Calcium	Ca	40.1	40
Carbon	C	12	12
Cerium	Ce	144.25	144
Chlorine	Cl	35.45	35.5
Chromium	Cr	52.1	52
Cobalt	Co	59	59
Copper (Cuprum) . .	Cu	63.6	63.5
Erbium	Er	166	166
Fluorine	F	19	19
Gallium	Ga	70	70
Germanium	Ge	72.5	72
Glucinum } same . .	{ Gl		
Beryllium } element . .	{ Be	9.1	9

List of the Elements—Continued

1	2	3	4
Gold (Aurum)	Au	197.2	197
Helium	He	4	4
Hydrogen	H	1.008	1
Indium	In	115	115
Iodine	I	126.97	127
Iridium	Ir	193	193
Iron (Ferrum)	Fe	55.9	56
Krypton	Kr	81.8	81.5
Lanthanum	La	138.9	139
Lead (Plumbum)	Pb	206.9	207
Lithium	Li	7.03	7
Magnesium	Mg	24.36	24
Manganese	Mn	55	55
Mercury (Hydrargyrum)	Hg	200	200
Molybdenum	Mo	96	96
Neodymium	Nd	143.6	143.5
Neon	Ne	20	20
Nickel	Ni	58.7	59
Niobium	Nb	94	94
Nitrogen	N	14.1	14
Osmium	Os	191	191
Oxygen	O	16	16
Palladium	Pd	106.5	106
Phosphorus	P	31	31
Platinum	Pt	194.8	195
Potassium (Kalium)	K	38.5	39
Praseodymium	Pr	140.5	140.5
Rhodium	Rh	103	103
Rubidium	Rb	85	85.5
Ruthenium	Ru	101.7	101.5
Samarium	Sm	150.3	150
Scandium	Cs	44.1	44
Selenium	Se	79.2	79
Silicon	Si	28.4	28

List of the Elements—Continued

1	2	3	4
Silver (Argentum) . . .	Ag	107.93	108
Sodium (Natrium) . . .	Na	23.05	23
Strontium	Sr	87.6	87.5
Sulphur	S	32.06	32
Tantalum	Ta	181	181
Tellurium	Te	127.6	127.5
Thallium	Tl	204.1	204
Thorium	Th	232.5	232
Tin (Stannum)	Sn	119	119
Tungsten (Wolfram) . . .	W	184	184
Uranium	U	238.5	238.5
Vanadium	V	51.2	51
Xenon	X	128	128
Ytterbium	Yb	173	173
Yttrium	Y	89	89
Zinc	Zn	65.4	65
Zirconium	Zr	90.6	90.5

Relation between the English system and the metric system of weights and measures:

1 gram = 15.432 grains.	1 ounce (avoir.) = 28 grams.
1 kilogram = 2.2 lbs. (avoir.)	1 lb. (avoir.) = .453 kilogram.
1 litre = 1.76 pt. = .88 qt.	1 qt. = 1.136 litre.
1 inch = 2.54 cm.	1 cm. = .39 inch = .4 nearly.

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Commonly Occurring Chemicals.
 Their Formulas and Chemical and Popular Names.

Oxide:

1. H_2O , Hydrogen Monoxide, Water.
2. H_2O_2 , " Peroxide,
3. MgO , Magnesium Oxide, Magnesia
4. CaO , Calcium Oxide, Quick Lime or, Stone Lime
5. HgO , Mercuric Oxide, Red Oxide of Mercury.
6. Al_2O_3 , Aluminium " Corundum / chief ingred of emery
7. CO , Carbon Monoxide, Carbonic acid gas.
8. CO_2 , " Dioxide,
9. SiO_2 , Silicon Dioxide, Silica, Quartz (Sand)
10. PbO , " Red Lead.
11. N_2O , Nitrous Oxide, Lathing gas.
12. N_2O_5 , Nitrogen Pentoxide, Nitric Anhydride.
13. As_2O_3 , Arsenic Trioxide, (White) Arsenic.
14. SO_2 , Sulphur Dioxide,
15. MnO_2 , Manganese Dioxide, Black Oxide of Manganese
16. Fe_2O_3 , Ferric Oxide, Iron Rust.

Sulphates

1. H_2SO_4 , Hydrogen Sulphate, Sulphuric Acid, Oil of vitriol
2. Na_2SO_4 , Sodium Sulphate, Glopers salt.
3. $CuSO_4$, Copper " Blue stone, Blue Vitriol, Copperas
4. $MgSO_4$, Magnesium " Epsom salt.
5. $CaSO_4 \cdot 2H_2O$, Hydrated Calcium Sulphate, Gypsum (plaster of Paris)
6. $ZnSO_4$, Zinc Sulphate, White Vitriol

7. $KAl(SO_4)_2 \cdot 12H_2O$ Potassium Aluminium Sulphate, Alum

8. $FeSO_4$ Ferrous Sulphate, Green Vitriol

Chlorides

1. HCl , Hydrogen chloride, Hydrochloric Acid
 NH_4Cl , Ammonium " Mariatic Acid
2. $NaCl$, Sodium " Common salt
3. $MgCl_2$, Magnesium " Impurity in salt common making it deliquescent
4. $HgCl$, Mercurous " Calomel
5. $HgCl_2$, Mercuric " corrosive sublimate
Bichloride of mercury

Carbonates

1. H_2CO_3 , Hydrogen Carbonate, Carbonic Acid
2. Na_2CO_3 , Sodium " washing soda
3. $NaHCO_3$, " Bi " saleratus
4. $KHCO_3$, Potassium " marble, limestone, chalk
5. $CaCO_3$, Calcium " white lead
6. $PbCO_3$, $Pb(OH)_2$ Basic lead "

Nitrates

1. HNO_3 , Hydrogen nitrate, nitric acid
2. $NaNO_3$, Sodium " Chili saltpetre
3. KNO_3 , Potassium " salt petre, nitre
4. $AgNO_3$, Silver " Lunar caustic
5. NH_4NO_3 , Ammonium nitrate



PRICE
40
CENTS